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DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

Fifteenth Six-Month Report
for the period
1 July 1970 - 31 December 1970

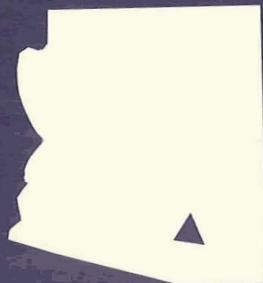
For the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Grant NGL-03-002-019

by

Stuart A. Hoenig
Principal Investigator

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ENGINEERING EXPERIMENT STATION
COLLEGE OF ENGINEERING
THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA

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I. INTRODUCTION, ABSTRACT AND SUMMARY

This report will cover the work performed from 1 July 1970 through 31 December 1970 on Grant NGL-03-002-019 between the University of Arizona and the National Aeronautics and Space Administration.

This contract was set up to support the development of new types of detectors for analysis of planetary atmospheres. Initially, the interest was in detectors for use under partial vacuum conditions; recently, the program has been extended to include detectors for use at one atmosphere and adsorption systems for control and separation of gases.

Results to date have included detectors for O_2 and H_2 under partial vacuum conditions (Publications 1, 3, 4). Experiments on detectors for use at higher pressures began in 1966, and systems for CO , H_2 , and O_2 , were reported in 1967 and 1968 (Publications 8, 12). In 1968 studies began on an electrically controlled adsorbent. It was demonstrated that under proper conditions a thin film of semiconductor material could be electrically cycled to adsorb and desorb a specific gas. This work was extended to obtain quantitative data on the use of semiconductors as controllable adsorbents (Publication 12).

In 1968 a new technique for dry replication and measurement of the thickness of thin films was developed. A commercial material, Press-O-Film was shown to be satisfactory when properly used. This

technique is most useful for studies of semiconductor thin films where normal interference techniques are not practical because of the non-reflective nature of the film (Publication 13).

In 1969 studies began on a corona discharge detector for water vapor. This system was shown to be rapid in response, suitable for continuous low power operation and reasonably linear in output (on a logarithmic plot) from 10% R.H. to 75% R.H. A program to develop this detector for agricultural applications began in 1970.

The electroadsorption phenomena reported in 1968 (Publication 12) was extended to bulk ZnO samples by using a gas chromatograph. The objective of developing a controllable electroadsorbent is slowly being realized.

Studies of the reaction between carbon monoxide and palladium have been under way since 1966. In 1970 this work was split into two separate programs; the first one is a study of gas-metal interactions with emphasis on catalysis. The second is a development of the CO/Pd system into a practical system for use by public health groups.

II. SUMMARY OF WORK IN THE PAST SIX MONTHS

A. Carbon Monoxide Detector

This program is now supported by the Environmental Control Administration rather than NASA and will therefore be discussed in Section E of this report. Here we shall only comment that the sensitivity of the CO detector is now 50 PPM. This is a great improvement over the 500 PPM previously reported.

B. Corona Discharge Humidity Detector

The current generated in a point-to-plane corona discharge has been shown to be dependent on the ambient water vapor pressure. The use of a multipoint brush and an ultraviolet source stabilizes the system and maintains sensitivity over a wide range of R.H. The system is being repackaged and tested for use in field studies. We have demonstrated that high ambient temperatures (50°C) do not affect the operation of the device. Improvement of the system to allow it to operate in the self-pumping mode will begin in the next six month period.

C. Surface Catalysis and Exo-Electron Emission

This is a very new program that is an outgrowth of our earlier studies of gas-surface interactions with the mass spectrometer. We have shown that when catalysis of the $\text{CO} + \frac{1}{2}\text{O}_2$ or $\text{H}_2 + \frac{1}{2}\text{O}_2$ reaction begins (on hot platinum) there is emission of nonthermal exo-electrons. This "exo-electron" emission can be used to monitor the progress of catalysis. There are definite indications that by controlling exo-electron emission we can increase or decrease the rate of catalysis.

D. Electroadsorption of O_2 on ZnO

Mr. Brad Frazier has left the program and this work is temporarily at a standstill. We are looking for a new graduate student to work on this program.

E. Other Activities in the Laboratory

The ARPA-sponsored studies on the relationships between fatigue and subsequent exo-electron emission are continuing. We have shown

that if a metal is fatigued to some fraction of its total life and then heated gently, it will emit exo-electrons. This electron current can then be related to the fatigue history of the specimen. We are also developing an exo-electron system for monitoring aircraft structures for development of cracks and crack growth during flight.

Mr. Michael Pomeroy has finished a wireless device to encourage student response in class. This work was supported by University of Arizona funds and used by Mr. Pomeroy as an undergraduate thesis project. A patent application on this device will be filed by Battelle Development Corporation in the name of the University of Arizona. At the moment Mr. Pomeroy is working with the U of A Medical College to develop a hand held defibrillator. This work is supported by College of Engineering funds.

Mr. Leland Payne is still using the laboratory for developing the various components of a State-wide Medical Telemetry System that will connect the various outlying community hospitals to the University of Arizona Medical School. This project will be used by Mr. Payne for his Ph.D. (EE) dissertation.

Another use of laboratory facilities occurs in connection with two courses taught by Professor Hoenig in Electronics and Instrumentation for graduate students in the Zoological, Geological and Medical Sciences. These students use the laboratory and its apparatus for demonstration and simple projects. This would be impossible without the long term support that we have received from NASA.

The laboratory is still used occasionally by members of the University of Arizona Lunar and Planetary Laboratory. We feel that this use of NASA supported facilities by another NASA funded project is an important example of how research funds can be conserved by joint use of facilities.

Mr. Robert Goetz has been working with the CO detection system. This carbon monoxide detector makes use of a palladium coil which is exposed to the radiation from a quartz ultraviolet lamp. The Pd wire is heated by DC current to about 400°C, this induces emission of positive ions (Na^+ , K^+). The ion current is a function of the partial pressure of CO. The reaction is quite specific, only H_2 or C_2H_4 have a similar effect.

The system is shown in figure 1. For test purposes a stream of tank CO flows thru a precision flowmeter and a rotary valve which acts as a chopper. (This chopper valve gives the CO input a square wave characteristic which helps in the calibration process). The CO flow is mixed with a controlled flow of house air and is passed thru a glass wool filter into the detector system.

The CO dissolves in the Pd lattice and increases the rate at which sodium or potassium impurity atoms diffuse to the surface. A fraction of these atoms are ionized by the high work function Pd surface and the UV light. The resultant K^+ and Na^+ ion current is attracted to a negatively biased screen collector and measured by an electrometer.

A recent calibration curve is shown in figure 2. The fact that we can detect CO at 50 PPM is significant, when we first reported

the CO detector the lower limit was about $1 \frac{7}{10}$ % CO by volume (10000 PPM. This improvement is the result of an intensive effort by Mr. Goetz and Mr. Pomeroy in the past year.

The ultraviolet light source has increased the signal to noise ratio and allowed us to drop filament operating temperatures to 400°C from 800°C . This will permit a great reduction in battery requirements when we design a portable system. Chopping the CO flow with a rotary valve (designed and built by Mr. C. Savitz) allows us to filter out the drift due to changes in house air-line pressure changes.

The system is being redesigned for packaging in a large attache case. The major problem is finding a suitable fan to draw air thru the detector. Even high quality spiral blowers seem to surge⁺ and this disturbs the DC level of the detector. We have ordered a miniature air pump and will test it in the near future. It is our expectation that careful design will make it possible to solve the surge problem. The portable system will be similar to that shown in figure 1. It is expected that 110V, 60 H_a power will be available. For truly portable applications a DC-DC charger-converter package will be supplied.

* This problem exists with all continuous monitoring detectors, in fixed installations baffles and surge chambers are used to solve the problem. Our portable system will require a special design to reduce the surge effects.

III. DETAILED PROJECT REPORTS

B. Corona Discharge Humidity Detector

Steven Bird

In our last report we discussed the repackaging of this detector in a sturdy metal container and presented a typical calibration curve for the 10% - 70% R.H. range. In the last six months we have built a heater system so that we could investigate the effects, if any, of high ambient temperatures. Summer temperatures over 115°F are not uncommon in Arizona deserts.

In the last six months the system has been redesigned for greater rigidity and resistance to leakage problems. Tests with the air preheater indicate that the device operates satisfactorily. Calibration with the Alnor Dewpointer has been satisfactory to about 70% R.H., above that value the Alnor accuracy is quite poor.

In the next six months we hope to obtain an improved calibration system (Cambridge Systems Model 880) from government surplus. Next semester Mr. Bird will start working with the U of A Agricultural School on field tests of the detector. A field system which would be self actuating, in terms of airflow, by means of the Electric-Wind-Effect.

The quartz tube generates its own airflow by means of the chimney effect using the heat dissipated by the UV light. The brush-screen system generates its airflow thru the corona discharge. Air and water ions of positive sign are produced and impelled toward the screen by the field of the brush. Collisions between ions and neutral gas molecules produce a general upward flow of air thru the humidity detector.

C. Surface Catalysis and Exo-Electron Emission

Fredoon Tamjidi

Mr. Richard Pope has finished his MSEE thesis in this area and the program has been taken over by Mr. Tamjidi. Mr. Popes thesis is attached to this report as an appendix.

In our last 6 month report we suggested, from preliminary experiments, that a connection existed between surface catalysis and exo-electron emission. This has been confirmed at least for the oxidation of CO or H_2 over hot Pd.

Obviously the phenomena of heterogenous catalysis is well known. For almost any gaseous reaction there are solids which increase or decrease the rate of reaction. Ample literature exists describing catalysts for specific reactions, but to date there is no general theory which explains why some catalysts accelerate a particular reaction and others do not, Reference 1. Because of the obvious commercial applications, the processes of catalysis have been studied in great detail with the hope of understanding the phenomena. A review of the historical background and theories is given by Reference 2.

In our experiments we have been looking at the emission of exo-electrons from the catalyst during reaction. The term exo-electron emission is used here to cover any form of electron emission other than the usual thermal, photoelectric or field emission effects. Exo-electron emission is observed whenever a solid surface is disturbed by alloying, sintering, grinding, melting, annealing, phase changes, or oxidation.

The idea that exo-electron emission might be related to catalysis follows from the work of Delchar (Reference 3) where it was shown that adsorption of oxygen on nickel induced exo-electron emission. If adsorption must precede catalysis, one might suspect that exo-electron emission would occur during catalysis. Further evidence for this phenomena might be found in the work of Lee (Reference 4). An AC electric field was shown to increase the rate of hydrogenation of benzene to cyclohexane over brass. The phenomena was very dependent on the frequency of the applied field but no explanation of the phenomena was proposed by the author. Sato and Seo (5) have followed the oxidation of ethylene to ethylene oxide over silver with exo-electron emission and demonstrated a linear relationship between the exo-electron current and the rate of ethylene oxidation. It is suggested that this type of relationship is a general one and can be used to follow catalytic reactions.

In view of the above one might expect that adsorption and catalysis on semiconductors would be affected by electric fields, as suggested by the work of Volkenshtein, Reference 6. Experimental verification of the effects of electrical fields on adsorption of O_2 on ZnO was reported by Hoenig and Lane, Reference 7. The effect of electric fields on semi-conductor catalysis has been reported by Standnik and Fentsik, Reference 8. They showed that the catalytic activity of AgO , for oxidation of methyl alcohol, could be controlled by external electric fields.

Because of the obvious commercial implications implicit in control of catalysis we chose to follow the rate of reaction with a

quadrupole mass spectrometer and look for exo-electrons with an electrometer.

APPARATUS

The apparatus is shown in figure 3. The mass spectrometer was an EAI - QUAD 250⁺. The catalyst was commercial platinum wire 0.010" in diameter. Catalyst temperatures were monitored by a thermocouple welded to the Pt wire. Electron currents were collected by a stainless steel collector biased at +24 volts, and measured with a Keithley 417 picoammeter. The Pt wire could be grounded or biased at various voltages by a Fluke 870 power supply.

Two reactions have been investigated to date, oxidation of CO or H₂ over hot Pt. In all cases an excess of O₂ was present. Typically the total pressure was about 6×10^{-6} Torr with a H₂ partial pressure of 1.5×10^{-6} Torr.

The vacuum system was a stainless UHV design with oil and ion pumping. Base pressure with the oil pump valved off was 5×10^{-9} Torr. The oil pump was only used for pumpdown; during experiments, the ion pump maintained the vacuum. Tests to determine if the ion pump was producing any signals in the electron measurement system were negative.

The gases were commercial grade taken from standard cylinders. The gas input was controlled by Granville-Phillips leak valves. Partial pressures were monitored by a discharge gauge and the Vac-Ion pump current.

⁺ Made available by the Jet Propulsion Laboratory thru the cooperation of Dr. Charles Giffin.

EXPERIMENTS AND RESULTS

The initial experiments on oxidation of H_2 will be discussed in some detail to indicate the procedure. The Pt filament was grounded and the collector was at +24 volts. O_2 and H_2 were admitted separately to a total pressure of $5 \cdot 10^{-6}$ Torr and the filament was heated from $20^\circ C$ to $900^\circ C$. During the heating only negligible electron emission was observed. The change in the $\frac{M}{e} = 18(H_2O)$ was quite small.

When both H_2 and O_2 were present there was some catalysis at room temperature but no exo-electron emission was observed. When the filament was heated to $775^\circ C$ catalysis began and, after a short delay exo-electron emission was observed. Typical results are shown in figure 4. Here the height of the H_2O peak (K) in arbitrary units and the exo-electron current (I_e) are plotted as a function of time. Notice that the electron current follows the rate of reaction until the rate of reaction (K) is constant at which point I_e drops to the base line value. This phenomena was quite consistent and a series of experiments at higher and lower filament temperatures indicated that the time for the sudden drop to occur decreased with increased filament temperature. For example at $800^\circ C$, (K) reached equilibrium in 7 minutes and I_e fell to the base line value. At $700^\circ C$ a longer time (15 min.) was required before (K) reached a constant value and I_e fell to the base line level. We tentatively suggest that the electron emission is due to the disturbance of the catalyst surface during the "induction period" when (K) is moving toward its equilibrium value. Emission of electrons from disturbed solid surfaces is well known

(Gruenberg Ref. 8). The erratic oscillations of the I_e signal are thought to be a real phenomena in the sense that the surface disturbance discussed above involves groups of atoms moving about on the catalyst itself. This mass motion is responsible for the escape of electrons from the catalyst.

The phenomena of mass motion in solid catalysis is often observed in catalytic processes. A fresh metal catalyst is usually relatively inactive. After a certain amount of use (the induction period), the catalyst reaches its greatest effectiveness. At this time the catalyst material is often found to be grooved and twisted indicating that extensive mass motion has occurred.

To restate the chain of reasoning, we suggest that the observed exo-electron emission is a measure of mass surface diffusion during the induction period when the catalyst is approaching its equilibrium condition.

It appears that once the equilibrium condition is established the surface is quite stable. Once (K) has reached a constant value, and I_e has fallen to the base line level, increasing the catalyst temperature does not change (K) appreciably and I_e does not increase. If the $(K = \text{constant})$, $I_e = \text{Base Level Point}$ is established, and the H_2/O_2 ratio is reduced to zero (at constant total pressure) the rate of catalysis (K) goes to zero but no increase in I_e is observed. This suggests that once the surface has been "formed" it remains in that condition even though the temperature increases and the actual rate of catalysis comes to a halt because one of the reactants has been removed.

At this point we decided to switch to the CO/O_2 reaction to

see if similar phenomena would be observed. This was indeed the case and in figure 5 we show a typical plot of K and I_e versus time for CO oxidation. The peak height (K) increases and then decreases to a constant value. The exo-electron current I_e follows (K) and drops to the base level when (K) reaches a constant value. In this experiment we continued to observe K and I_e until after the filament has been turned off. In figure 5 we notice that when the filament is turned off a short burst of electrons is observed. This is not a switching transient (the decay time is far too long). We will show later that the decay time depends upon the filament bias in a complex fashion. The burst of exo-electrons as the filament cools is thought to be due to surface migration as the filament relaxes to its room-temperature equilibrium condition.

It was felt important to see what effect, if any, would occur if we biased the filament to reduce or enhance exo-electron emission. For these experiments the filament was raised to a constant temperature and biased with the Fluke power supply to ± 2.8 volts.

The first experiments indicated that changing the filament bias during a catalysis run did change the value of I_e. However, the value of K was unaffected. This suggested that exo-electron emission was related to surface migration during the catalytic induction phase but that there was no direct connection between electron emission and catalysis itself.

This idea was found to be incorrect when we tried applying the bias voltage to the filament before heating it to begin catalysis. This is shown in figure 6, a -28 Volt bias increased both (K) and I_e over the no-bias values. A +28 volt bias decreased both (K) and I_e

below the "no-bias" values. This effect is very difficult to explain in terms of our suggestion that exo-electron emission is due to surface migration. Here it appears that a relatively small voltage $\pm 28 \text{ V}$, applied before the catalyst is heated, can radically modify the exo-electron emission and the rate of reaction. One would expect field induced surface effects at voltages of say 5 to 10 KV, but at 28 volts-- this seems very strange.

Further evidence of this effect is shown in the next figure 7. Here (K) was observed at a whole range of voltages. In each case the bias was applied with the filament at 20°C . Then the catalyst was heated to 770°C and held at that temperature until (K) was effectively constant. At this time the heating current was removed and the filament cooled to 20°C .

As we expected the higher voltages yielded higher (K) values. More surprising is the way in which (K) rises (upon heating) and falls (upon cooling). At high voltages (-83V) the rise is rapid and the drop is preceded by a steep pulse which dies away very rapidly. At (-30V) the rise occurs much more slowly and the decay is significantly longer. There seems to be some sort of surface change which depends upon the filament voltage both in absolute value and rate of formation and decay.

A similar experiment at a series of positive filament bias voltages indicated that +28 volts reduces both I_e and K. Increasing the filament bias in steps to +80 volts reduced I_e to almost zero but had no effect on K. Apparently the effect of a positive filament bias on the rate of catalysis (K) is complete at 28 volts. In

contrast K increases with negative filament bias up to about 100 volts.

There is direct evidence that a positive filament bias not only reduces K but it conditions the filament against catalysis. Evidence of this effect is shown in figure 8. Here we have plotted (K) versus time for a filament that was first biased at + 30 volts to retard exo-electron emission. The filament was cooled to 20°C and -30V was applied. An increased value of (K) was observed but it was significantly lower than that usually observed at -30V. We suspected that the + 30V exposure had somehow "formed" the catalyst into an ineffective state. The catalyst was heated to 950°C in vacuum without any applied potential, then cooled to 20°C. The -30V was reapplied and the catalytic run repeated. The value of (K) was that normally observed with -30V potential suggesting that the +30V potential had "formed" the catalyst and the heating at 950°C had "annealed" the material.

At this point we can only conclude that application of voltages as low as 28 volts can somehow change the effectiveness of the catalyst for this reaction.

It is apparent that we are far from understanding this whole electrocatalytic process especially since it seems to depend upon the rate at which the filament is heated to the operating temperature. As an example of this, we show in figure 9 the normal behavior of (K) and I_e (heavy dashed line) that is observed if the filament is heated to 800°C in about 0.3 seconds. If instead the filament is heated slowly for some 45 seconds, to attain 800°C, the rate of

reaction (K) goes up then dies away again while I_e shows no change at all. This suggests that a sudden temperature change is required to induce the surface migration that leads to exo-electron emission. One might postulate that some sort of thermal supersaturation must exist before the reaction can occur.

CONCLUSIONS

It should be apparent that no real conclusions can be drawn at this point. We have demonstrated that for at least two catalytic reactions it is possible to control the rate of reaction by externally applied electrical fields. The possibility of extending this technique to various commercial catalytic reactions is justification for continuing the studies.

Improved equipment has been constructed for this experiment. We are now able to work with three different filaments alternately without opening the vacuum system. Particular attention will be devoted to the reaction of ammonia with oxygen, over platinum, to produce NO and NO₂. Another interesting reaction is that CH₃OH with oxygen, over silver, to produce H₂CO. These topics will be investigated by Mr. Tamjidi for his MSEE thesis.

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PERSONNEL

Students who have been supported by the grant and their present activities are listed below:

1. Donald Collins, M.S., 1963, Ph.D., California Institute of Technology, Sept. 1969. Presently Research Associate, CIT.
2. George Rozgonyi, Ph.D., 1963. Senior Staff Member, Bell Telephone Laboratories, Murray Hill, New Jersey.
3. Donald Creighton, Ph.D., 1964. Professor, University of Missouri, Rolla. (Partial NSG-458 support).
4. Maj. C. W. Carlson, M.S., 1965. Active duty, U.S. Army.
5. Melvin Eisenstadt, Ph.D., 1965. Associate Professor, University of California, Santa Barbara.
6. John Lane, M.S., 1968. Philco Ford Company, Tucson.
7. William Ott, M.S., 1970. Burr-Brown Research Company, Tucson. (Partial NASA support).
8. Richard Pope, M.S. 1970. Hewlett Packard Corporation, Palo Alto, California.

PUBLICATIONS GENERATED TO DATE BY RESEARCH ON THIS GRANT

S. A. Hoenig and Others

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FIGURES

1. CO Detector System
2. Response of CO Detector
3. Exo-Electron Catalysis System
4. Catalysis and Exo-Electron Emission versus Time
5. CO₂ Peak (K) and I_e versus Time, Oxidation of CO
6. Effect of Filament Bias on K and I_e During Oxidation of Carbon Monoxide
7. Effect of Various Filament Voltages (-) on Catalytic Oxidation of CO
8. Effect of Previous Exposure to Negative Voltage on Catalysis of CO Oxidation
9. Effect of Rate of Heating of the Filament from Room Temperature to 800°C at the Start of the Reaction

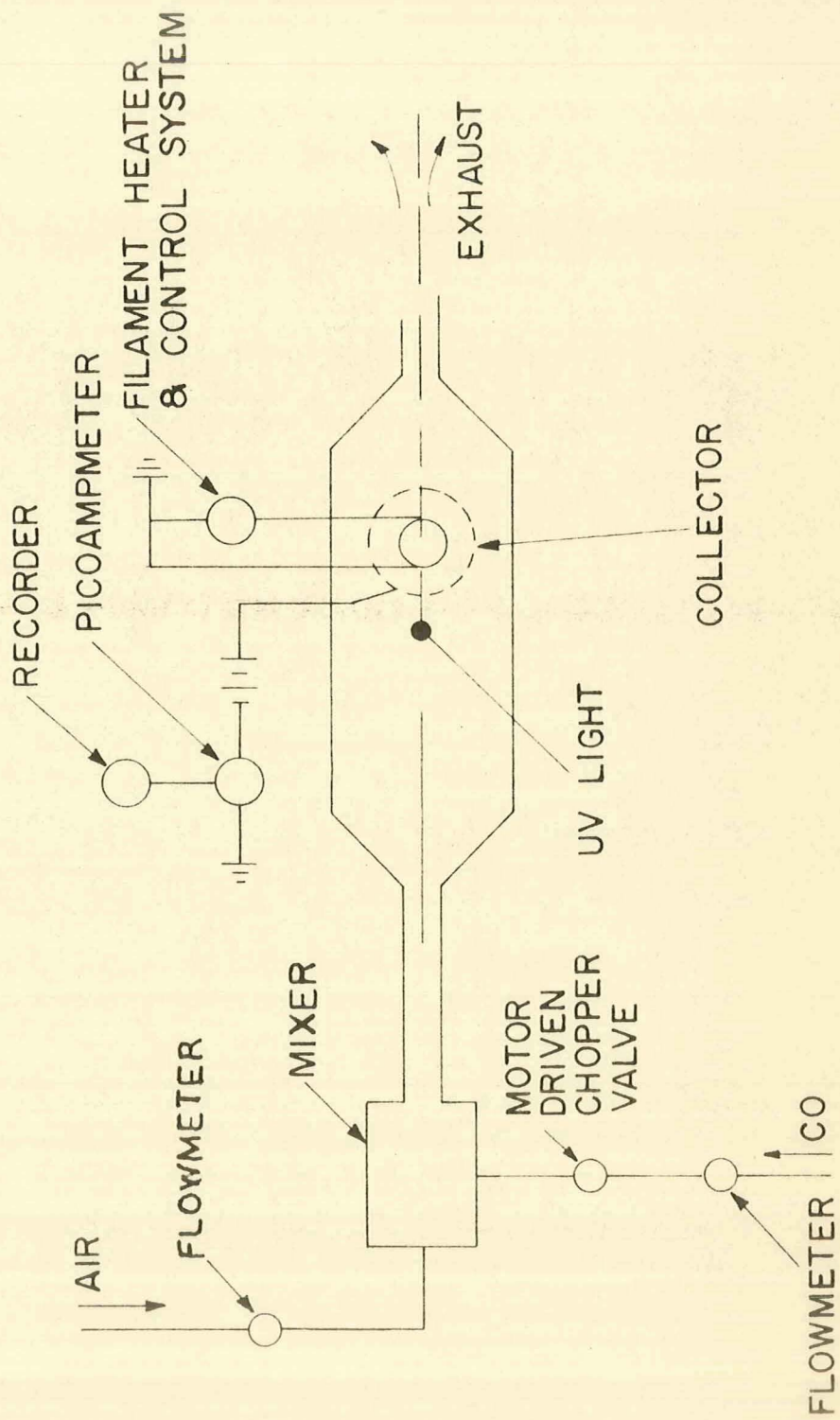


FIGURE 1. CO DETECTOR SYSTEM

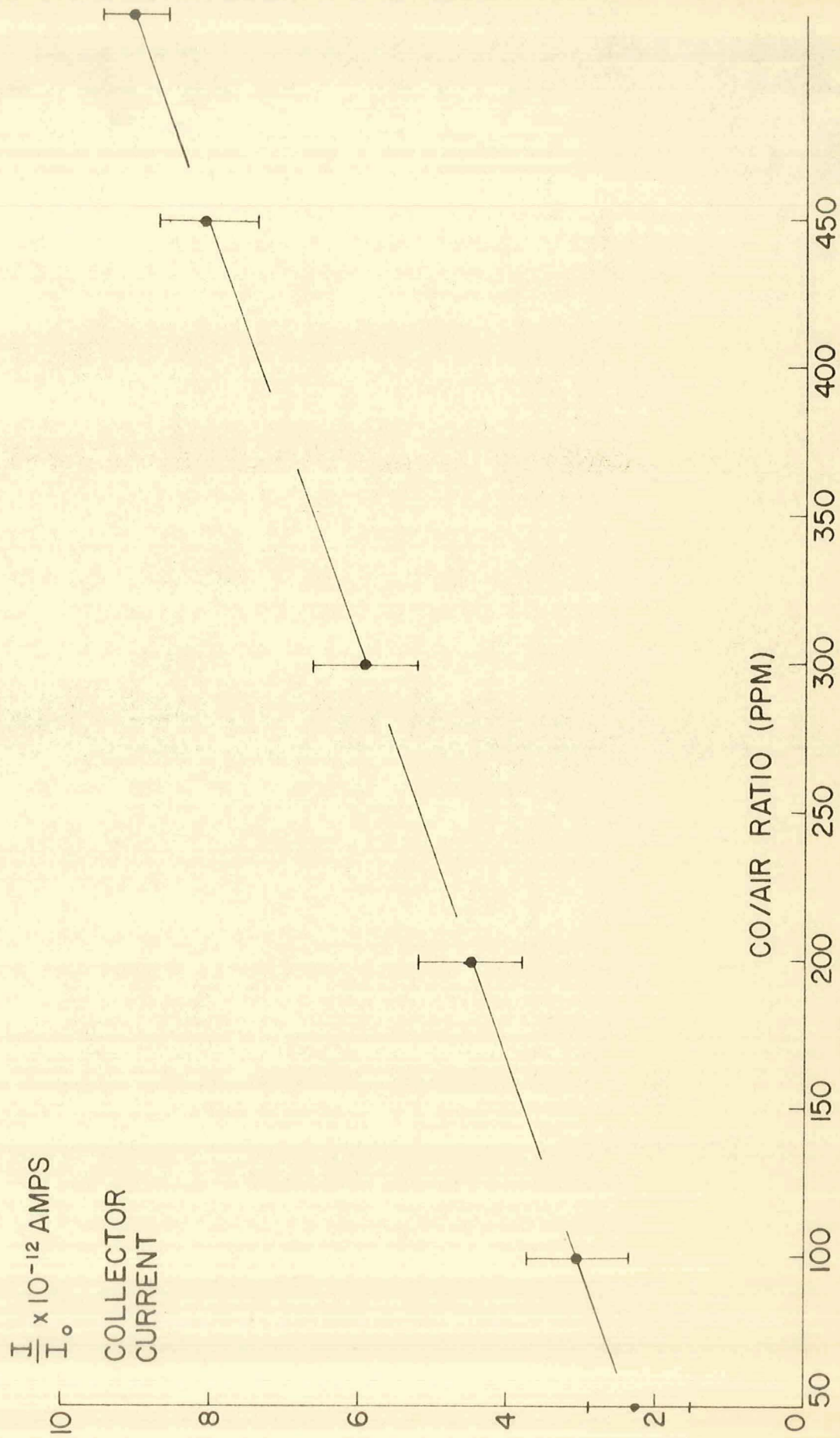


FIGURE 2. RESPONSE OF CO DETECTOR

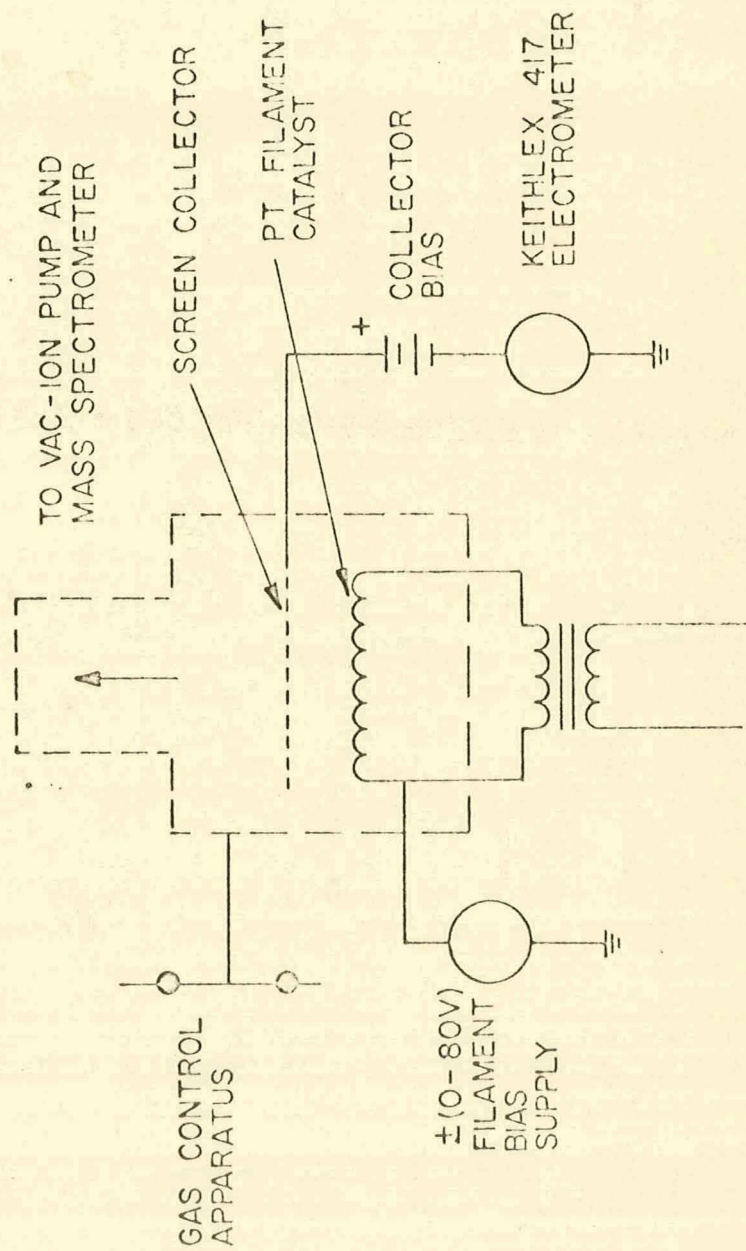


FIGURE 3. EXO-ELECTRON CATALYSIS SYSTEM

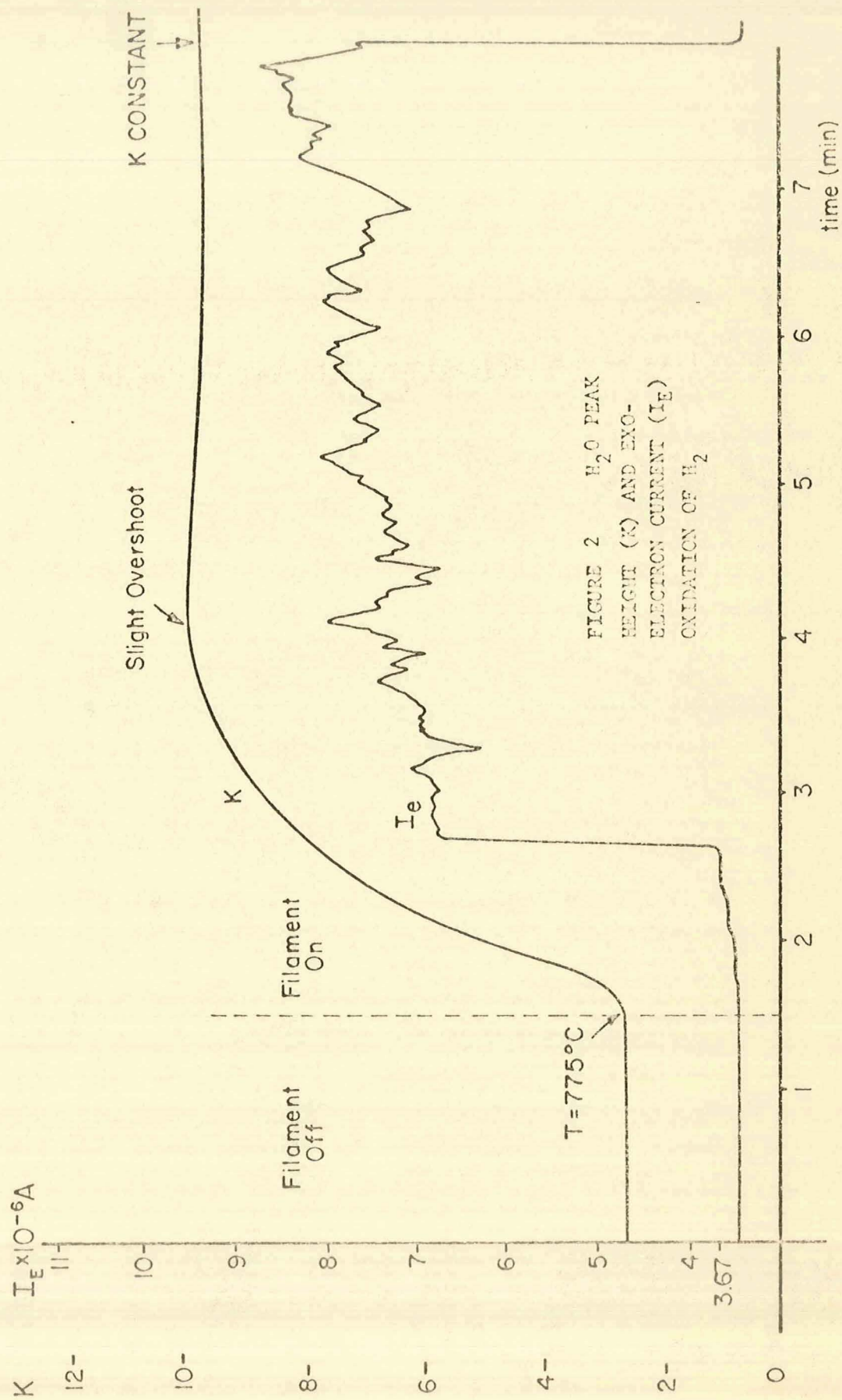


FIGURE 2 H₂O PEAK
HEIGHT (K) AND EXO-
ELECTRON CURRENT (I_E)
OXIDATION OF H₂

FIGURE 4. H₂O PEAK HEIGHT (K) AND EXO-ELECTRON CURRENT (I_E) OXIDATION OF H₂

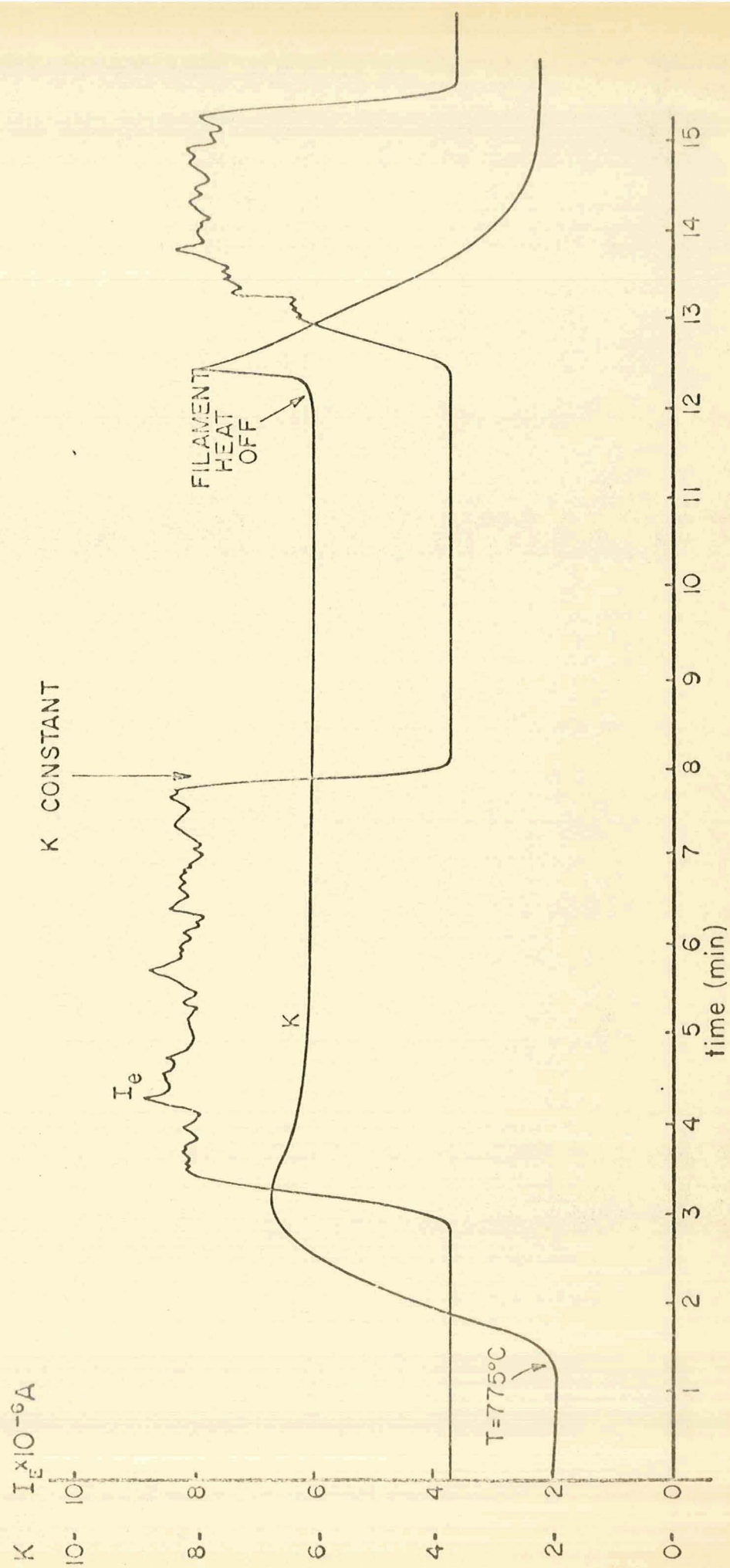


FIGURE 5. CO₂ PEAK (K) AND I_E VERSUS TIME OXIDATION OF CO

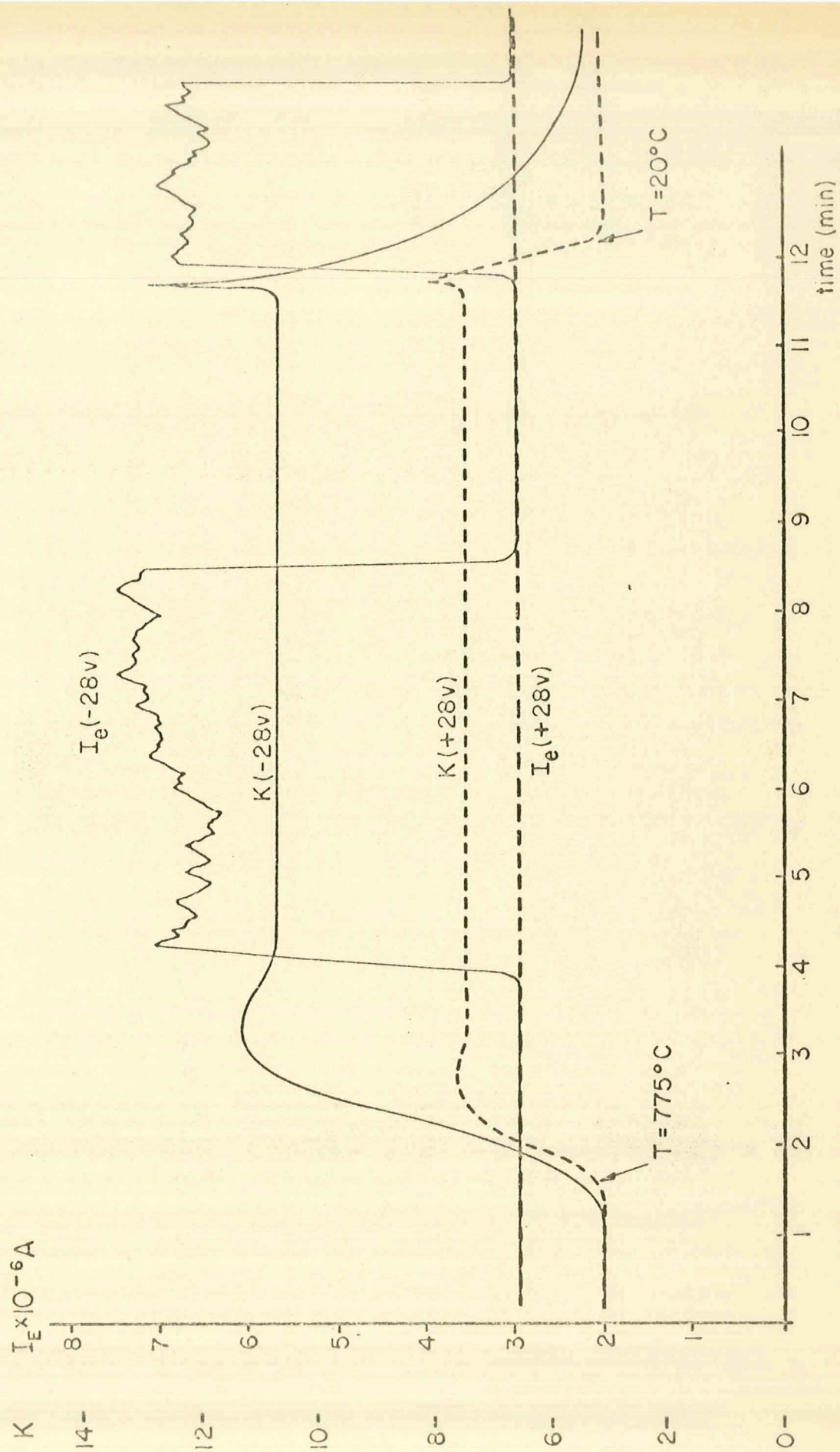


FIGURE 6. EFFECT OF FILAMENT BIAS ON K AND I_E DURING OXIDATION OF CARBON MONOXIDE

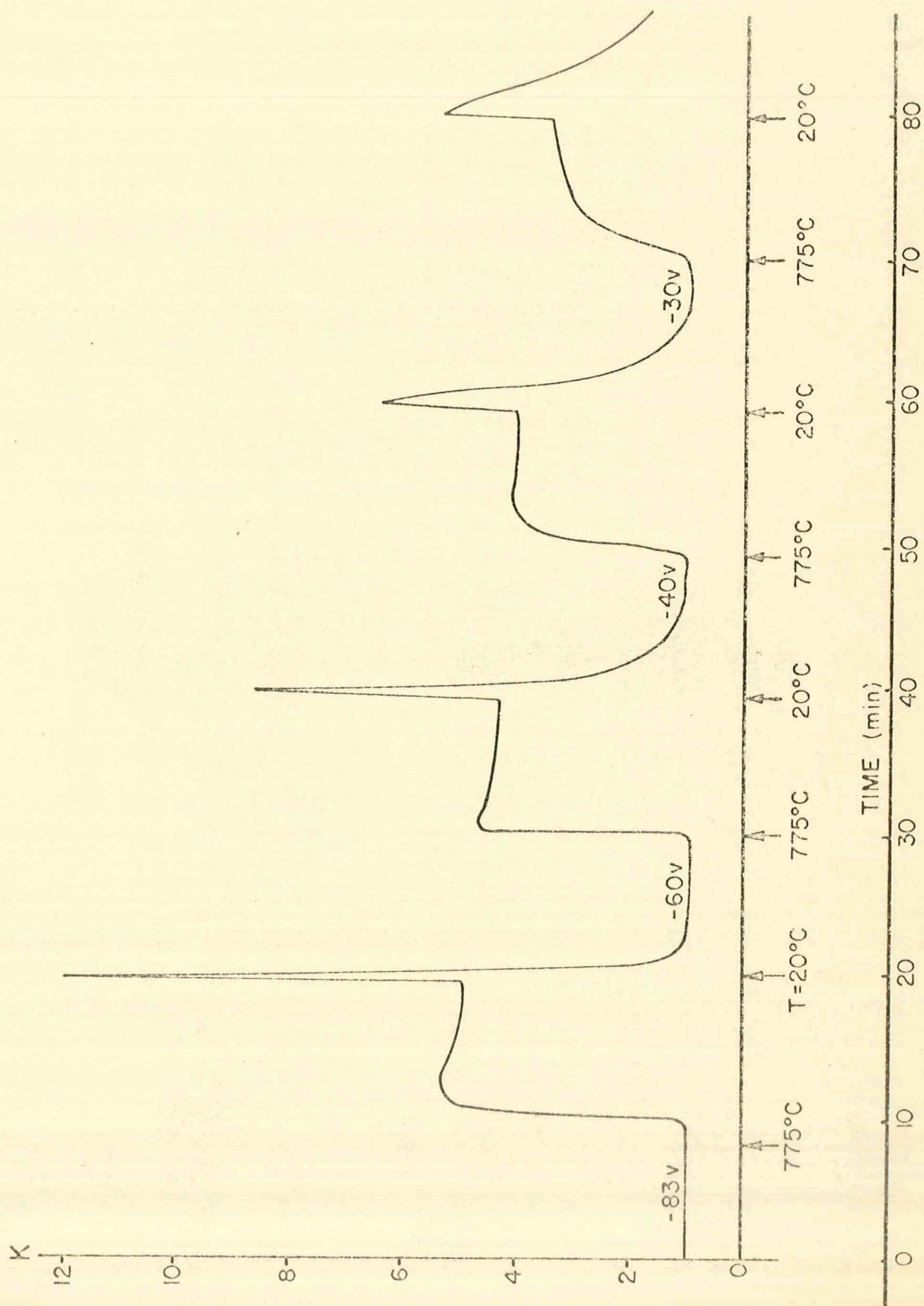


FIGURE 7. EFFECT OF VARIOUS FILAMENT VOLTAGES (-) ON CATALYTIC OXIDATION OF CO

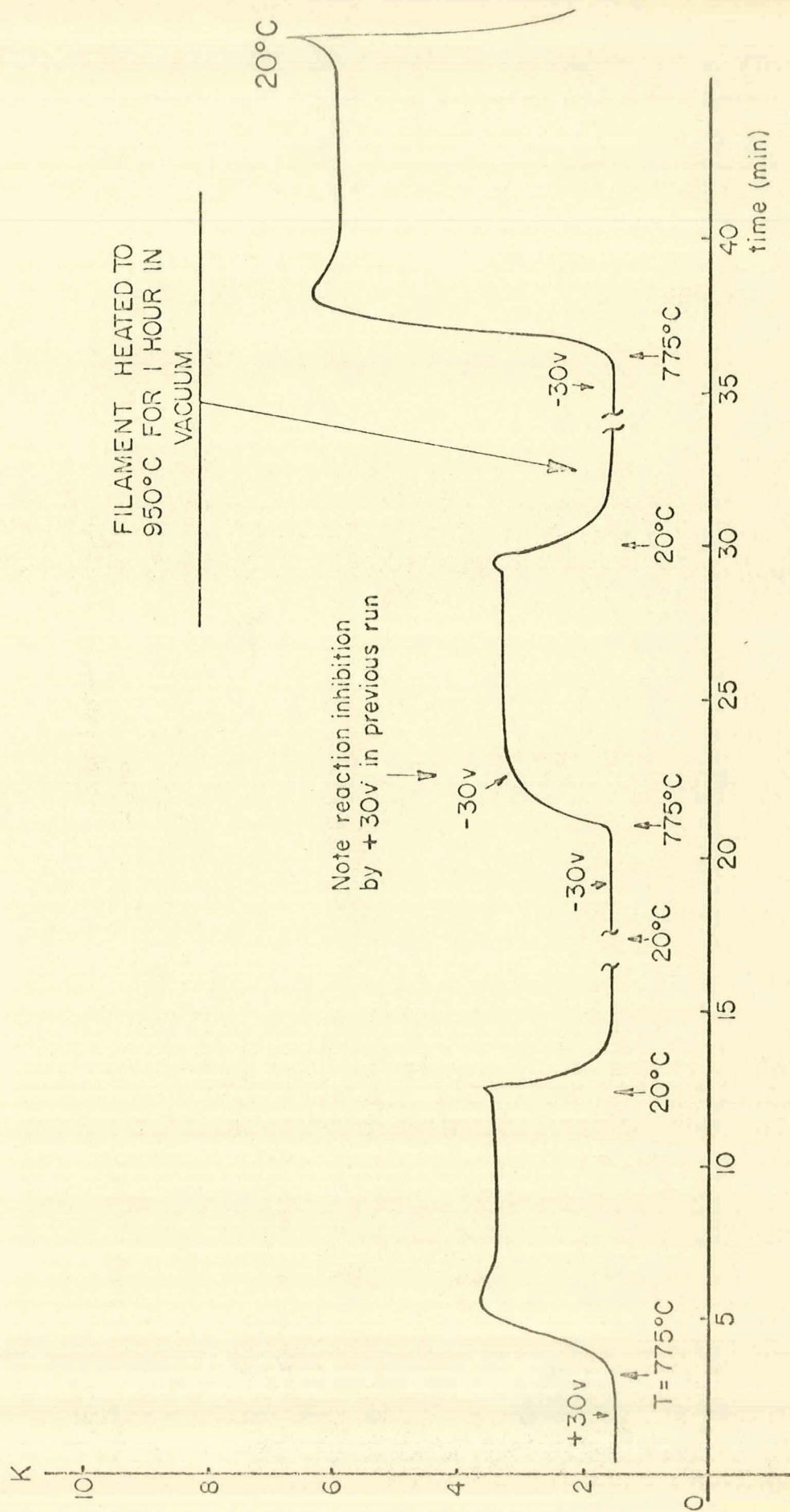


FIGURE 8. EFFECT OF PREVIOUS EXPOSURE TO NEGATIVE VOLTAGE ON CATALYSIS OF CO OXIDATION

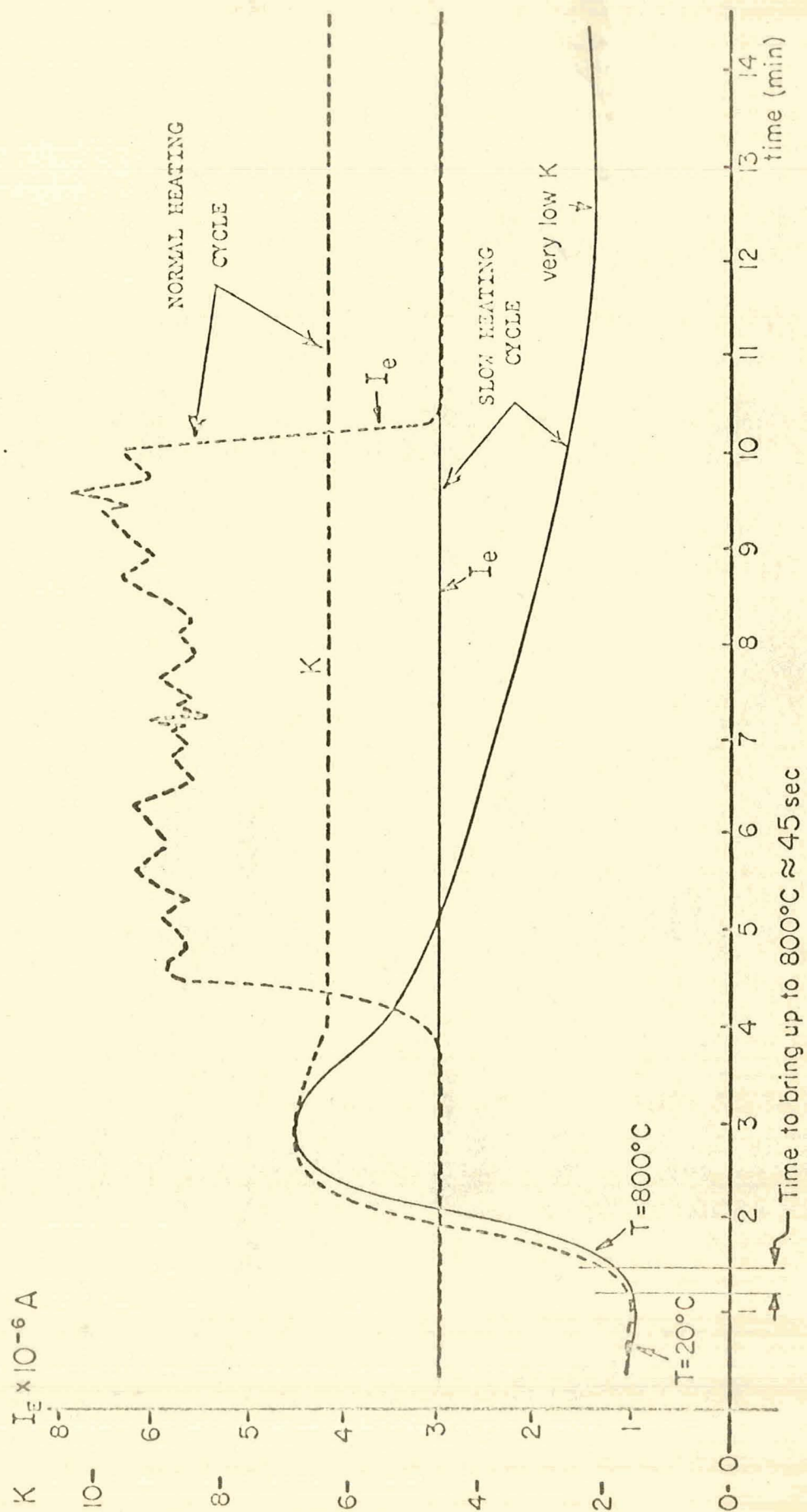


FIGURE 9. EFFECT OF RATE OF HEATING OF THE FILAMENT FROM ROOM TEMPERATURE TO 800°C AT THE START OF THE REACTION (Fil. Bias = -15 volts)

APPENDIX

POSITIVE ION EMISSION FROM PALLADIUM
(EFFECTS OF SELECTED AMBIENT GASES)

by

Richard A. Pope

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PREFACE

Surface effects have had a profound influence in electrical engineering, particularly in the area of solid state devices. Surface contamination of silicon crystals, electron induced migration of thin films, and sodium contamination are a few examples of phenomena that are essentially surface controlled.

One of the earliest problems in the manufacture of silicon solid state devices was surface contamination. One effect of this contamination was the occurrence of low resistive leakage paths across the surface of the silicon. In extreme cases this would render the affected device useless. Fortunately, this problem has been alleviated to a large extent by passivating the surface with a layer of silicon dioxide.

Electron migration is a somewhat newer problem. The desire for more compact circuits has made Large Scale Integration very attractive. However, as the number of devices grew, the size of the metallic interconnections has shrunk correspondingly. With this decrease in size the current densities have increased proportionally. Under these high current densities the electrons tend to move defects in the metal interconnections. These defects collect at points of highest current density causing opens, or in some cases, causing metallic whiskers to grow out of the interconnections causing shorts to adjacent interconnections (Black 1969).

The problems associated with sodium contamination have been brought about by the development of the Metal-Oxide-Silicon, or MOS, transistor. One of the reasons for the long term drift observed in MOS transistors is sodium contamination of the silicon-silicon dioxide interface (Schlegel, Schnable, Schwarz and Spratt 1968). At least part of this contamination comes from the sodium impurities present in the aluminum evaporated onto the gate, and from the tungsten boats used to evaporate the aluminum (Hoenig 1967). Once the aluminum gate has been deposited, the sodium migrates out of the metal into the silicon dioxide insulator where it sets up a boundary layer of charge at the interface. This boundary layer acts like a bias on the gate and induces a shift in device characteristics. Later work (Hoenig and Pope 1968) has shown that a significant percentage of these contaminants can be removed during the aluminum evaporation by introducing an electric field gradient which draws sodium ions away from the semiconductor substrate.

These are by no means all of the ways that surface effects have become important in electrical engineering. These were picked both as a representative sample and in the case of the sodium contamination, to bear a direct relationship to the work presented herein.

The author is deeply indebted to many people for help in various stages of this work. In particular the author would like to thank the other graduate students in the lab, Brad Frazier, Bob Goetz, and Bill Ott, for their various suggestions during all phases of the experiments.

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ABSTRACT

An experimental system has been developed to investigate positive ion emission from palladium and the effects of ambient gases. A theoretical model is discussed and the probable causes of variations from this model are explained. Surface contaminants are found to be the major contributing factor to these anomalies.

CHAPTER 1

INTRODUCTION

It has been known for many years that all metals will emit charged particles when heated. Depending on the temperature of the metal and the impurities present, either positive or negative particles will be emitted (Quisenberry 1967). At low temperatures positive ion emission predominates while at temperatures approaching the melting point of the metal, thermionic emission of electrons takes place. In this study we will limit our discussion to the emission of positively charged particles.

Some of the behavioral characteristics of positive particle emission are generally accepted. When metals (i.e., Fe, Ni, Co, W, Mo) are first heated to about 650°C, a weak emission of sodium and potassium ions results (Brady and Zemany 1952; Smith 1929), with minor currents of caesium and rubidium. Regardless of temperature, it has been shown that none of the ions are from the parent metal itself (Barnes 1932). If the metal is heated rapidly and then held at constant temperature, the emission will reach a high value and then decrease exponentially with time to a lower constant value. When the metal is maintained at a constant temperature and gases are admitted to the system, the emission can either increase or decrease, depending on the type of gas and the temperature of the metal (Hoenig, Carlson, and Abramowitz 1967).

Although these phenomena are accepted as correct, one very obvious characteristic of the early experiments was the fluctuation in experimental data and the difficulty in getting repeatable results. Even with all the recent developments in ultrahigh vacuum systems and advances in instrumentation, the data are still very variable from experimenter to experimenter (Lichtman 1965). It is hoped that this work will explain some of the causes of this fluctuation in the data and open new areas of study towards an explanation of the mechanism of positive ion emission.

CHAPTER 2

POSITIVE ION EMISSION

Review

The study of positive ion emission is by no means new. Basic studies of the phenomena began in the early nineteen hundreds after the initial discovery of positive currents from metals (Richardson 1903, 1911). During the next three decades experiments were done on the effects of various gases (Bangham 1929; Bloch 1927) and on the identity of the particles emitted (Smith 1929; Whalen 1929). From about 1933 to the early 1950's very little work was done in this area.

Starting in the early 1950's a few investigators picked up the work. The first of the new investigators studied the effects of more complex gases (Brady and Zemany 1952). Some work was done during this time on explaining the mechanism of surface ionization (Ionov and Zanberg 1959). These attempts at finding suitable explanations for the phenomena were generally involved trying to fit the data to the Saha-Langmuir equation (Chupakin, Bibikova, and Polyakov 1967), with rather poor results.

The 1960's brought a flood of work concerning positive ion emission, the bulk of the work being done in Russia with a few scattered experiments done in Britain and the United States. Most of the work done in this area was directly concerned with an explanation

of the mechanism of surface ionization (Chupakin et al. 1967; Tinder, Antypas, and Donaldson 1964; Fogel, Rekova, and Kolot 1962; Rekova, Fogel, and Aleksandrov 1966). As with earlier work most of the effort was used trying to make the Saha-Langmuir equation fit the experimental data, with some success in a few cases (Chaikovskii, Pyatigorskii and Ptitsyn 1966).

Despite the studies discussed above, the physical basis of the phenomena is not yet clear even in a quantitative way.

Theory

In most cases the ions emitted from hot metals are ions of the alkali metal impurities already present in the host metal. Therefore in forming a workable theory to explain the positive ion emission, two factors must be considered; the effects of the diffusion of the impurities to the metal surface and the ionization process at the surface of the metal.

As was mentioned in Chapter 1, when metals are first heated to some fixed temperature there is an initial surge of current which then falls exponentially to a lower and constant value. This initial surge of current is due to the ionization of the impurities which have gathered at the surface of the metal before heating. Once the impurities which were present at the surface have been removed, the constant ion current is supplied by new impurities diffusing through the parent metal to the surface. It can be shown that this constant ion current will remain constant for quite some time. For example, given a ten

gram sample of 99.999% purity platinum, where half of the impurities are assumed to be alkali atoms; if an ionization current of 100 μA were maintained, it would take 10^9 seconds to exhaust the platinum of all its alkali impurities.¹

It has been suggested (Fogel et al. 1962; Tinder et al. 1964) that the impurity atoms travel along defects in the crystal lattice of the parent metal. Thus, if by some process (e.g., adsorption) the crystal lattice was expanded, creating new defects or enlarging the existing defects, the rate of diffusion and ion emission would increase.

We can show that a change in the diffusion would directly effect the flux of impurities by a simple argument if we assume that impurities traveling through the metal obey Fick's Law of Diffusion. Van Bueren (1961) has noted that the activation energies for dislocation diffusion along these dislocations can be represented by Fick's Law using a diffusivity D_g which is very much larger than the diffusivity of the bulk material.² For a hypothetical one dimension case, the

1. 10^7 seconds = 1 year.

2. Van Bueren cites an example on page 432 of copper diffusing into Si or Ge. In the absence of dislocations the diffusion of Cu into the diamond lattice is quite slow, but if sufficient dislocations exist the diffusion occurs very rapidly.

concentration of the impurities diffusing from a constant planar source through the material will have a solution of the form³

$$N_1(x,t) = N_0 \operatorname{erfc} \frac{y}{2\sqrt{D_g t}}$$

where:

$N_1(x,t)$ = Concentration of impurities as a function of time and distance into the host metal

y = Distance into the host metal

D_g = Diffusivity; combination of line defect diffusivity and bulk diffusivity

t = Time

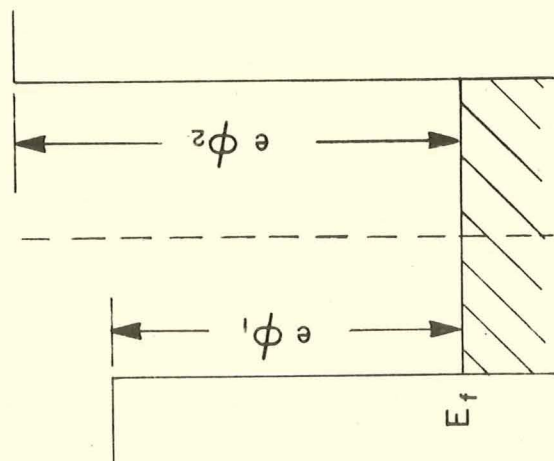
Studies of the diffusion of impurities through silicon and germanium crystals have shown that the diffusivity is an exponential function of temperature. This leads us to assume that the diffusion of impurities through metal crystal lattices would also be a function of temperature. Combining this dependence with the work done by Van Bueren, we can see that the flux of impurities to the surface of the metal will be dependent on both temperature and the condition of the crystal lattice.

Once the impurities have diffused to the surface the ionization mechanism must be accounted for. Following the development of

3. This solution will be recognized by many electrical engineers as the solution for impurities diffusing into homogeneous semiconductor material. In fact, the only difference is the line defect diffusivity, D_g , which will be much larger than the bulk diffusivity used for homogeneous crystals.

Quisenberry (1967), an intuitive grasp of this mechanism can be developed very easily. If palladium is used as the host metal with potassium as its single impurity, the argument is simplified considerably. It will also be assumed that the host metal is being heated in a vacuum. Since the host metal and the impurity atoms are in chemical equilibrium, the Fermi energy level is continuous across the system (Pariser 1964). The energy diagrams for this system are shown in Figure 1.

As the temperature of the system is increased the impurities which have migrated to the surface of the host metal will gain kinetic energy. If the temperature of the metal is raised high enough these impurity atoms will try to desorb as neutrals or positive ions. The probability of ionization is dependent on the difference between the work function of the palladium surface and the ionization potential of the impurity. Since palladium has a work function of 4.97 eV and potassium has an ionization potential of 4.32 eV, there is a distinct probability that the potassium valence electron will be lost to the host metal, forming a positive potassium ion. Once this ion gains sufficient energy to overcome image field forces it will be released from the surface of the palladium. The ionization of the impurity atoms has been shown to have a high probability whenever the ionization potential of the impurity is less than the work function of the host metal (Stuhlinger and Seitz 1960).



E_f = FERMI ENERGY LEVEL
FOR SYSTEM IN
EQUILIBRIUM

ϕ_n = WORK FUNCTIONS

Figure 1. Impurity-parent Metal Fermi Levels in Equilibrium

Basic Emission Equations

If it is assumed that the parent metal is in a vacuum, we can define the degree of ionization, α as

$$\alpha = \frac{N_+}{N_0}$$

where:

N_+ is the number of ionized impurities emitted for the surface of the host metal.

N_0 is the number of unionized impurities emitted from the surface of the host metal.

If we also assume the host metal has a uniform work function over its entire surface, the surface is not contaminated by impurities, and there are no external fields; then the degree of ionization can be expressed by the simple Saha-Langmuir equation

$$\alpha = \frac{g_+}{g_0} \exp \left(\frac{e(\phi - I)}{KT} \right)$$

where:

$\frac{g_+}{g_0}$ = Statistical weights of the ionic atomic states

e = Electron charge

ϕ = Work function of the host metal

I = Ionization potential of the impurity atom

K = Boltzman's constant

T = Temperature

For the alkali atoms the statistical weights g_+/g_0 is equal to $1/2$ since the ion is found in only one state while the atom has two states due to electron spin.

This equation has been developed by using a number of assumptions which do not hold under many practical situations. Variations of work function with temperature, the possibility of non-uniform work functions, and the distinct possibility of a contaminated metal surface are factors which have been ignored, and which could affect the accuracy of the results. Even if we assume that variations of work function with temperature are small, and if we assume variations in work functions across the surface of the host metal will average out, the possibility of contamination of the metal surface should be taken into account.

Referring back to the work in Quisenberry (1967) we can again develop an intuitive grasp of the effect of various surface layers on the Saha-Langmuir equation. The necessary changes in the equation will arise from both the presence of alkali atoms on the surface and from surface contamination due to gases or other impurities.

The effect due to the alkali atoms is caused by a surface potential set up by the alkali ions before they are desorbed from the surface of the host metal. If we assume a layer of strongly bonded alkali atoms on a planar surface of the host metal, we can approximate the surface potential (Quisenberry 1967) by

$$\phi_{s1} = \frac{\sigma_1 \mu_1 \theta_1}{\epsilon}$$

where:

ϵ_0 = Permittivity of free space

σ_1 = Number of available bonding sites for alkali atoms

μ_1 = Dipole moment of an ion-image combination

θ_1 = Degree of coverage, less than 1

This surface potential will lower the effective value of the work function of the metal. Taking this change into account we now have a modified Saha-Langmuir equation of the form,

$$\alpha = \frac{g_+}{g_0} \exp \left(\frac{e\phi - eI - e\phi_{s1}}{KT} \right)$$

It has been shown, again by Quisenberry (1967), that if this surface potential is as low as 3 volts, the degree of ionization becomes almost negligible.

The effect of the alkali atoms can be compounded at temperatures less than 100°K. At these temperatures the surface coating can be several layers deep (Bradley and Ruedl 1962). This can cause the work function of the metal surface to be replaced by that of the alkali atoms.

The effects on the work function by various gases can be handled in the same manner. As the gases are passed over the surface of the metal a certain portion of the mixture will be adsorbed onto the surface (Brady and Zemany 1952). The possibility for an electron to transfer from the surface of the metal to the adsorbed gas will

certainly exist. If enough of these negative ions are formed and are adsorbed onto the metal surface, a surface potential would result. We can approximate the surface potential by the dipole equation

$$\phi_{s2} = \frac{\sigma_2 \mu_2 \theta_2}{\epsilon_0}$$

where the terms are the same as in the previous case, except they now refer to the adsorbed gas.

The net effect of this surface layer would be determined by the type of gas and the metal involved. If the gas is a strongly electropositive gas,⁴ such as hydrogen, the surface layer should act in the same manner to the alkali layers and inhibit the degree of ionization. An electronegative gas, on the other hand, would tend to enhance the degree of ionization. These effects, however, are dependent on both the condition of the metal surface and the degree of coverage of the metal by the adsorbed gas.

A third effect which has been largely ignored until now is due to other contaminants on the surface of the host metal. It has been assumed in the past that most contaminants would be desorbed from the metal very rapidly at the temperatures required for positive emission. However, Palmberg and Tracy (1966) noted that even at high temperatures, there were strongly held contaminants on the surface of

4. Electropositivity refers to the tendency of an element to donate an electron during reactions while electronegativity infers acceptance of an electron.

palladium. The majority of these contaminants were found to be sulfur and carbon and were thought to be bulk impurities of the palladium ribbon used in the experiments. Removal of these contaminants was accomplished by sputtering the surface of the palladium with a 7 microamps/cm² beam of 400 eV argon ions for 50 hours. After this time only minute amounts of sulfur and carbon were detected.

Several researchers have noticed effects due to surface contamination. Chaikovskii, et al. (1966) blamed non-uniformities in the platinum ribbon used for the discrepancies in the ionization potentials he observed. However, any variations due to different crystal faces should average out and give reasonably close results. It seems likely that the variations noticed by Chaikovskii, et al. (1966) were due to contamination of the platinum surface. Wilson and Ivanetich (1964) recorded variations in the work function minus ionization potential of -1 to +.8 electron volts. They also mentioned that this variation could be due to contamination. It seems likely, therefore, that contamination will be found on the surface of the metal.

CHAPTER 3

DESIGN OF EXPERIMENTAL SYSTEM

Vacuum System

The vacuum system consisted of a stainless steel vacuum chamber, a Welch Duo-Seal rotary mechanical pump, a 300 watt Consolidated Vacuum Corporation oil diffusion pump, a 50 liter/second Varian Vac-Ion pump, and two pressure gauges.

The mechanical pump was used mainly to back the diffusion pump, except during the low vacuum experiments where it was used alone to pump down the system. For the high vacuum experiments the diffusion pump was used to bring the system into the Vac-Ion pump range where the Vac-Ion pump would take over. Pressures at or below 10^{-7} torr were achieved with no bake out of the system.

The gases admitted to the system during the experiments were controlled by two Granville-Phillips leak valves. The system pressure was monitored by a Vacuum Industries discharge gauge for the high vacuum experiments, and by a Pirani gauge for pressures in excess of 5 microns.

Mass Spectrometer

An Electronics Associates, Incorporated quadripole 250 mass spectrometer was used to monitor the gases and ions in the system during the experiments. With this mass spectrometer, 95% resolution of all mass peaks up to 90 AMU was easily obtained.

Ionizer Assembly

The ionizer assembly is shown schematically in Figure 2. Electrical connections to the assembly were made through a Varian high vacuum connector. The AC current used to heat the filament was supplied through an isolation transformer to enable the filament to be biased at potentials above or below AC ground. An alumel-chromel thermocouple was used to monitor the filament temperature. A Leeds and Northrup potentiometer was used to measure the thermocouple potential, making it possible to detect temperature changes of $\pm 5^{\circ}\text{C}$ at 1000°C .

Mechanical support for the filament was supplied by the field box shown in Figure 2. The field box was electrically isolated from the filament by a pair of Teflon spacers so it could be biased with respect to the filament.

Ion currents from the filament were detected by a stainless steel screen collector just below the field box. The currents were measured by a Hewlett-Packard 425A picoammeter and, in some cases, recorded by Heathkit chart recorders.

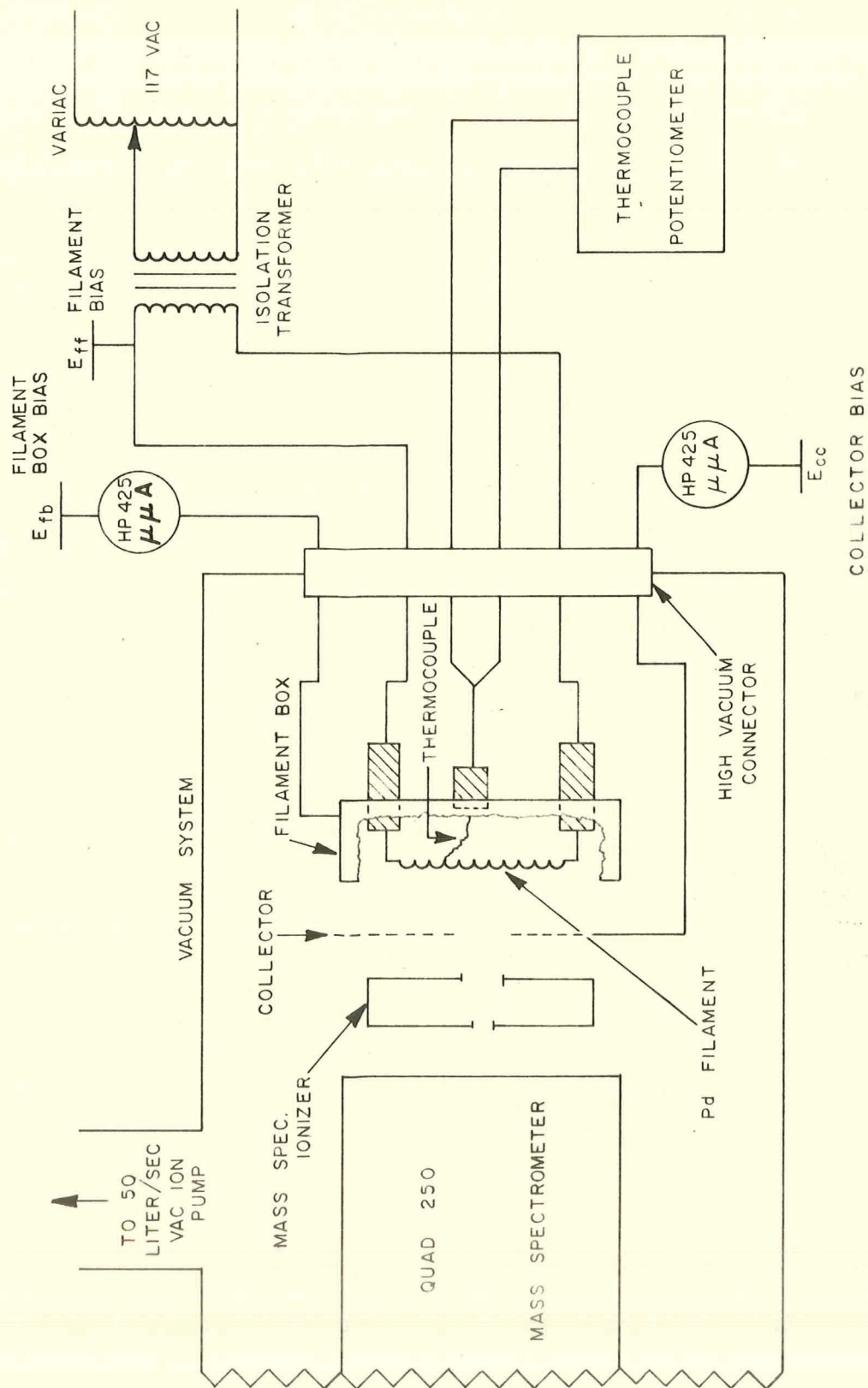


Figure 2. Experimental System

CHAPTER 4

EXPERIMENTS

During this investigation of positive ion emission, three separate experiments were performed; they involved first ion emission in partial vacuum, second effects of gases and gas pressures, and third effects of contamination.

Throughout these experiments palladium was used as the ion emitter. Palladium was used because it has a high work function (4.97 eV) which approaches that of platinum while its cost is significantly lower than that of platinum.

The temperature of the palladium was held at 800°C throughout the experiments. Previous work (Hoenig et al. 1967) indicated that this temperature gave the best signal to noise ratio for positive ion emission from palladium.

The gases used in the experiments were commercially available at a purity level of 99.995%. The mass spectrometer was used to monitor the gas mixtures in the vacuum system.

Ion Emission in Partial Vacuum

This series of experiments was designed to investigate the atomic species that were being ionized on the palladium filament. To simplify detection of these ions, the Quad 250 ionizer shown in Figure 2 was removed. The filament was biased at + 20V to accelerate particles

directly into the quadripole assembly. It was found that the velocity of the ions into the quadripole was not critical for operation of the mass spectrometer.

In the first experiments the system was pumped down to a base pressure of 10^{-7} torr. The mass spectrometer was turned on as soon as the pressure reached 10^{-5} torr and allowed to stabilize during the rest of the pumping cycle. Once the base pressure had been reached, the palladium filament was heated to 800°C and the mass spectrometer swept from 0 AMU to 65 AMU.

The second set of experiments was designed to find if the gases, which were to be used in later experiments, were being ionized on the palladium. The same sequence as above was used except the system was pumped down and flushed several times to 10^{-5} torr with the gas to be tested, before the filament was heated.

Effects of Gases and Gas Pressures

Two gases were initially used in the early experiments, hydrogen and oxygen. These gases were picked to determine what effects two chemically very different gases would have.

For these experiments the collector was connected to the filament box and biased at 10V with reference to ground. The filament itself was connected to ground. The system was pumped down to 10^{-7} torr and the filament was heated to 800°C .

The emission was first allowed to stabilize in vacuum, and then measured. The gases were admitted both individually and together

via the leak valves, and the emission was again allowed to stabilize for three to five minutes before being measured.

The second part of this experiment was designed to detect variations of emission with gas pressure. Nitrogen was used in addition to hydrogen and oxygen to determine if chemical reactions had an effect on emission.

The system was first pumped down to .01 mm pressure using the roughing pump only. The system was flushed several times with the gas to be tested, and allowed to pump down after each flushing. Once a pressure of .01 mm had again been reached the filament was heated to 800°C and emission allowed to stabilize. The gas was then admitted in small steps over 5 decades of pressure. At each data point the filament temperature was adjusted to compensate for the heat dissipated by the gas and the emission was allowed to stabilize for five minutes before measuring.

Effects of Surface Contamination

In an effort to check the possibility of contamination on the surface of the palladium, experiments were run to see if these contaminants could be removed by reaction with hydrogen or carbon monoxide. These gases were used because they are known to form compounds with both carbon and sulfur, and because H₂ and CO are known to increase the ion current from hot palladium (Hoenig et al. 1967).

The system was first pumped down to 10⁻⁷ torr by the Vac-Ion pump and the filament, and the collector grounded. The gas used was

admitted to the system by the leak valves and the pressure was reestablished at 5×10^{-6} torr. The ionizer of the mass spectrometer was then turned on and allowed to operate continuously during the experiment.

Once several background spectra had been recorded the palladium filament was turned and allowed to reach 800°C. The spectra was monitored continuously for any changes in peak height.

CHAPTER 5

EXPERIMENTAL RESULTS

As we have seen in Chapter 3, there are three possible mechanisms which might affect positive ion emission:

1. Changes in the palladium work function.
2. Changes in the alkali ion impurity diffusion rate.
3. Surface contamination which interferes with alkali metal ionization.

The results of our experiments indicate that all three mechanisms have an effect on the rate of ion emission. No one mechanism, however, can be singled out as the major influence. As an indirect result of the investigation other questions relating to positive ion emission have also been explored. These will be mentioned as they arise below.

Positive Ion Emission in Partial Vacuum

The first series of experiments involved observing the emitted ion spectrum from hot palladium as a function of time. The results are shown in Figure 3. It is interesting to note that while the cesium and potassium peaks remained constant, the sodium peak diminished with time. This aging of the sodium peak has been noticed by Rekova, Strel'chenko, Fogel, and Kwa Sun-Shan (1962).

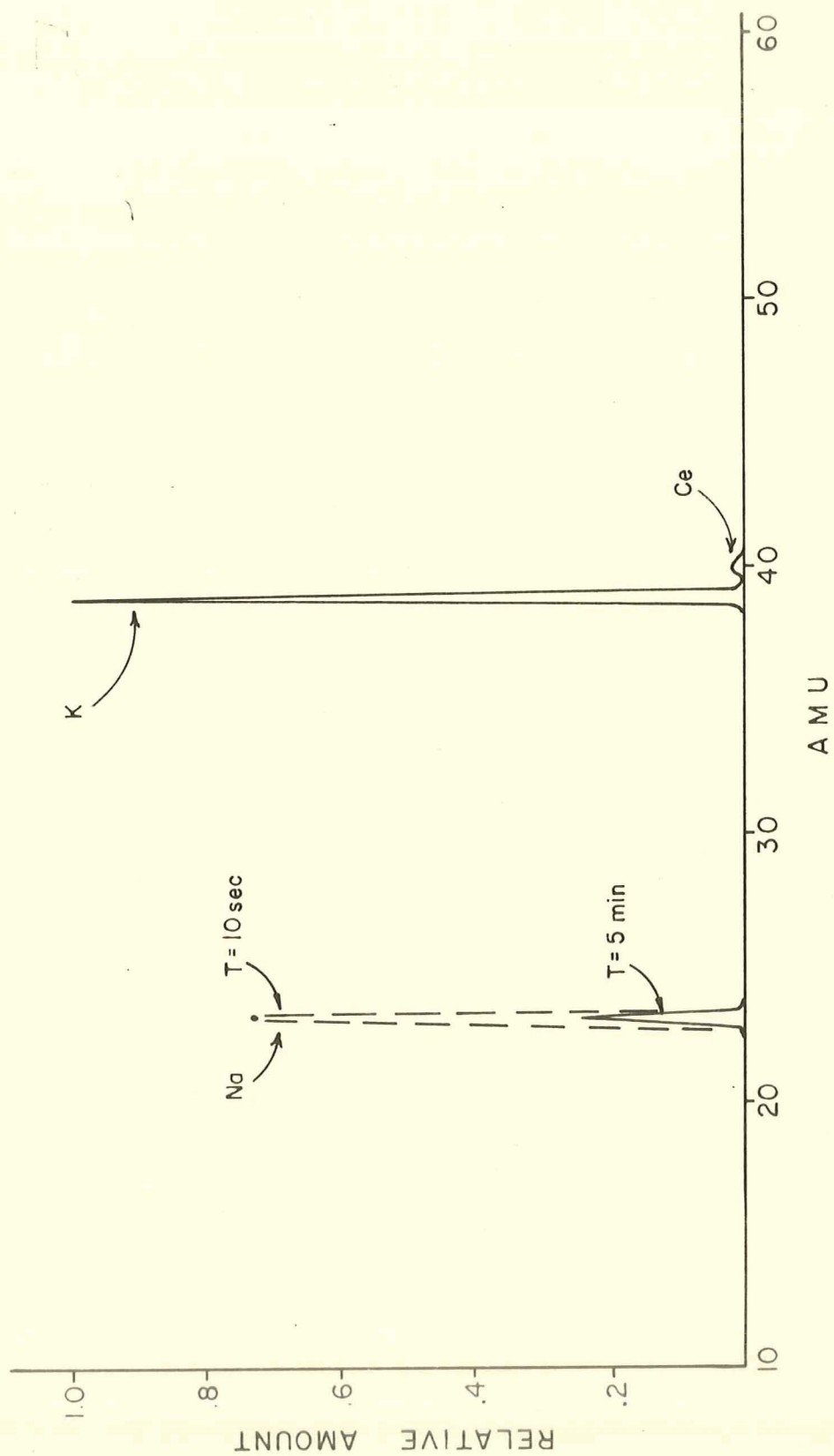


Figure 3. Variation of Ion Spectrum with Time

The initial high level of sodium ion emission suggest that sodium accumulates at the palladium surface at room temperatures by diffusing along grain boundaries in the palladium. The burst of ions seen when the palladium is first heated represents the ionization of this surface concentration. The lower, constant value, reached after five minutes is then due to the steady state rate of sodium impurity diffusion to the surface.

A second aspect of this experiment was that the only detectable ions were of the alkali elements. Bachman and Silberg (1958) investigated the question of the ion species emitted by hot palladium. Using rather crude apparatus, they observed what appeared to be ions of both the hydrogen atom, H^+ , and the hydrogen molecule, H_2^+ , when they exposed hot palladium to hydrogen. In our experiments we monitored the ion species emitted by the hot palladium as various gases were admitted. It was found that at no time were any gases ionized, and at no time were ions other than those of the alkali metals observed.

Effects of Gases and Gas Pressures

The changes in total positive ion current, from palladium at 800°C, due to the sequential admission of hydrogen and oxygen are shown in Figure 4. It is interesting to note that both hydrogen, an electro-positive gas, and oxygen, an electronegative gas, caused an increase in the emission current. The increase due to the hydrogen is surprising in that it is exactly counter to what is predicted by a change in work function in the Saha-Langmuir equation.

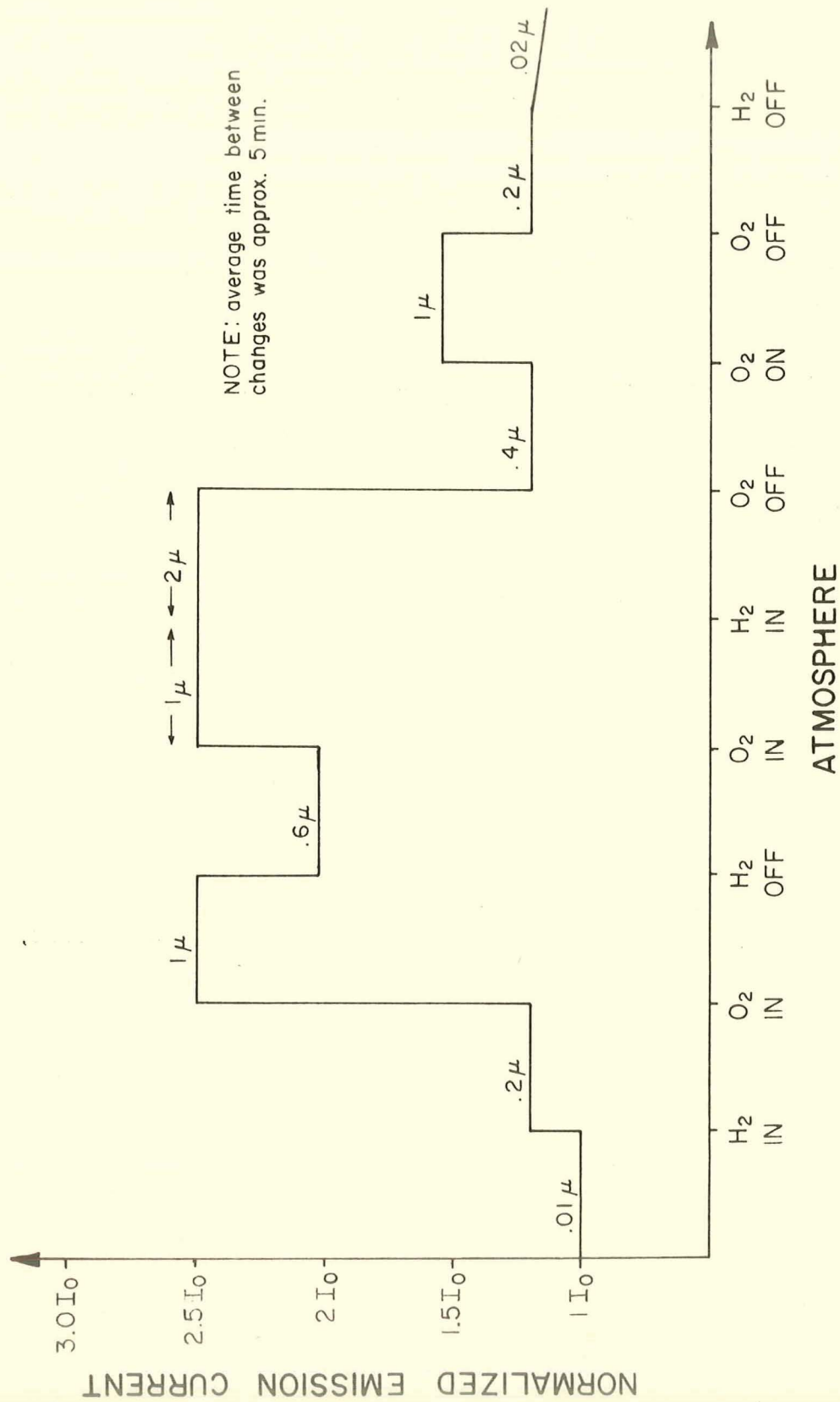


Figure 4. Emission Current vs. Atmosphere

Rekova et al. (1966) noticed an increase in emission current when oxygen was admitted to hot platinum at 800°C. However, they also noticed that the temperature of the platinum was increased to 1100°C, the admission of oxygen caused the total current to decrease.

The temperature threshold of 1100°C seen by Rekova et al. (1966), and the increases in emission due to hydrogen cannot easily be explained by a change in work function argument. However, a plausible explanation for these phenomena can be developed in terms of the surface contaminants found on palladium by Palmberg and Tracy (1966). At temperatures above the threshold the oxygen and hydrogen adsorbed by the palladium could react with the contaminants and be desorbed as compounds. However, below this threshold the adsorbed gases would either have too little energy to combine with the contaminants, or after reacting have too little energy to leave the surface of the metal. In either case, at low temperatures the two gases would suppress positive ion emission while at higher temperatures they would tend to enhance the emission. This agrees, at least in principle, with the effects noticed in this experiment. This hypothesis is explored further in the last section of this chapter.

The second series of experiments involved the variation of total emission current as a function of the partial pressure of hydrogen, oxygen, and nitrogen (Figures 5-13). The most significant observation is the hysteresis observed in all current versus pressure plots. These curves have a marked resemblance to adsorption-desorption curves

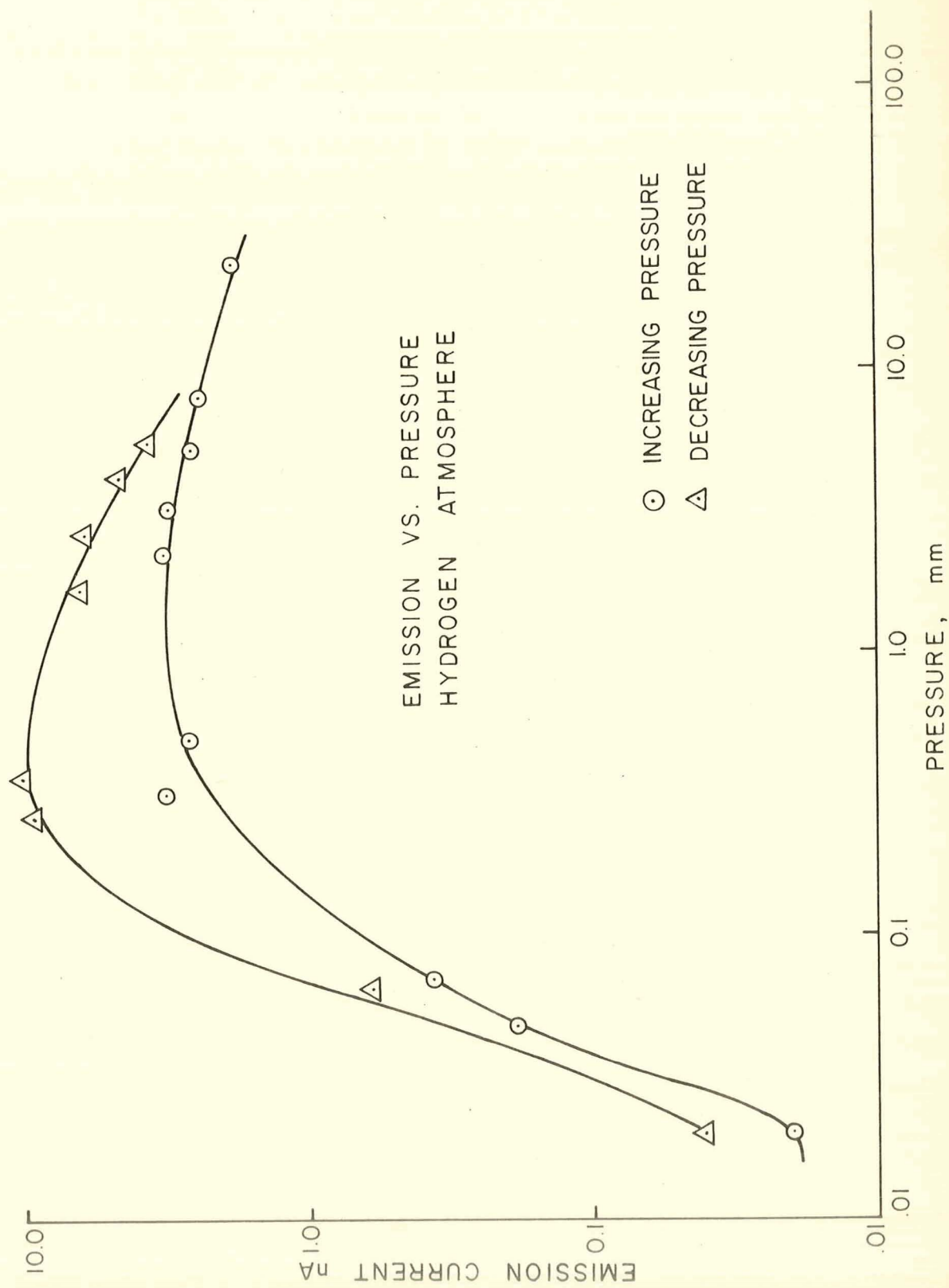


Figure 5. Emission vs. Pressure Hydrogen Atmosphere, Run I

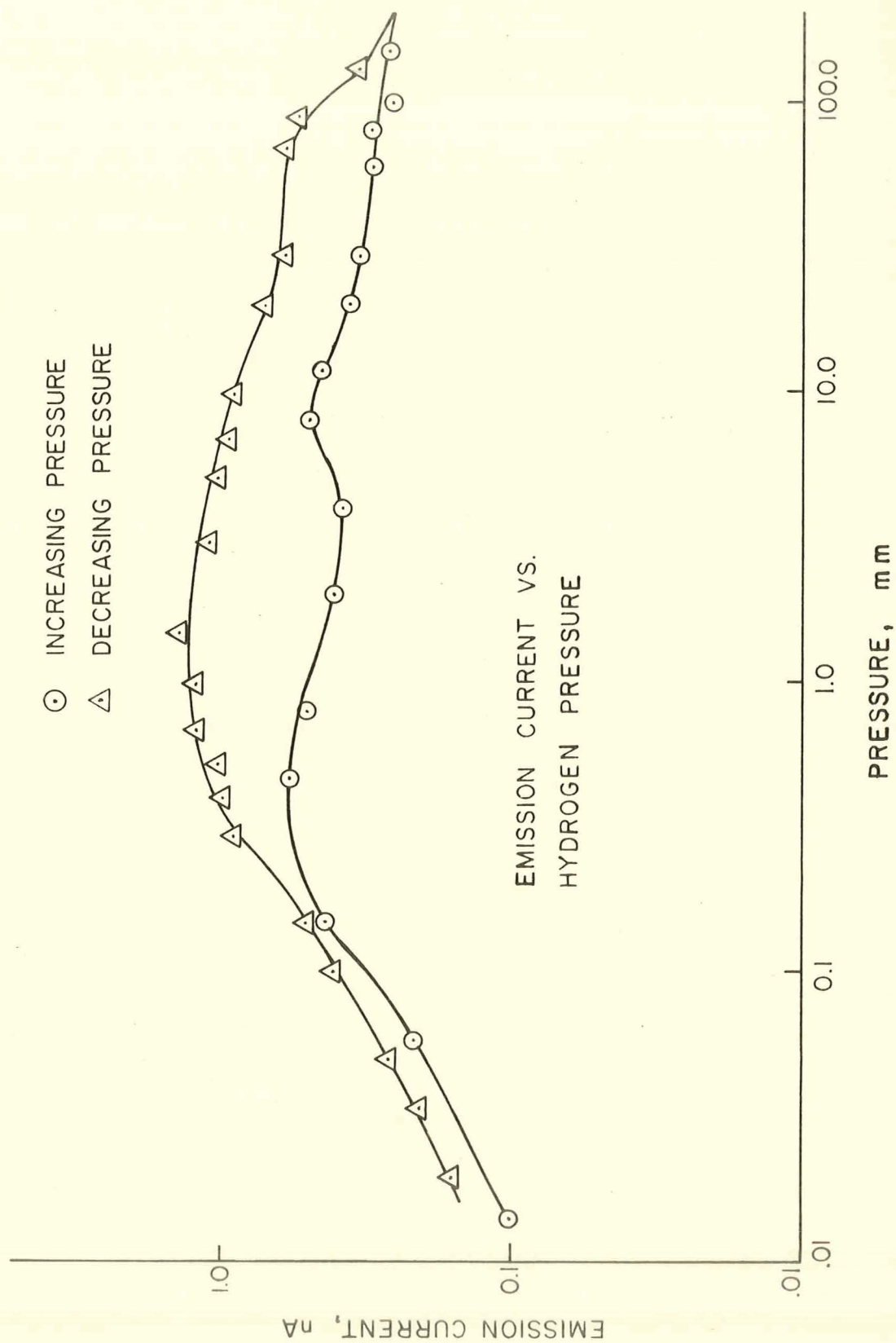


Figure 6.. Emission vs.. Pressure Hydrogen Atmosphere, Run II

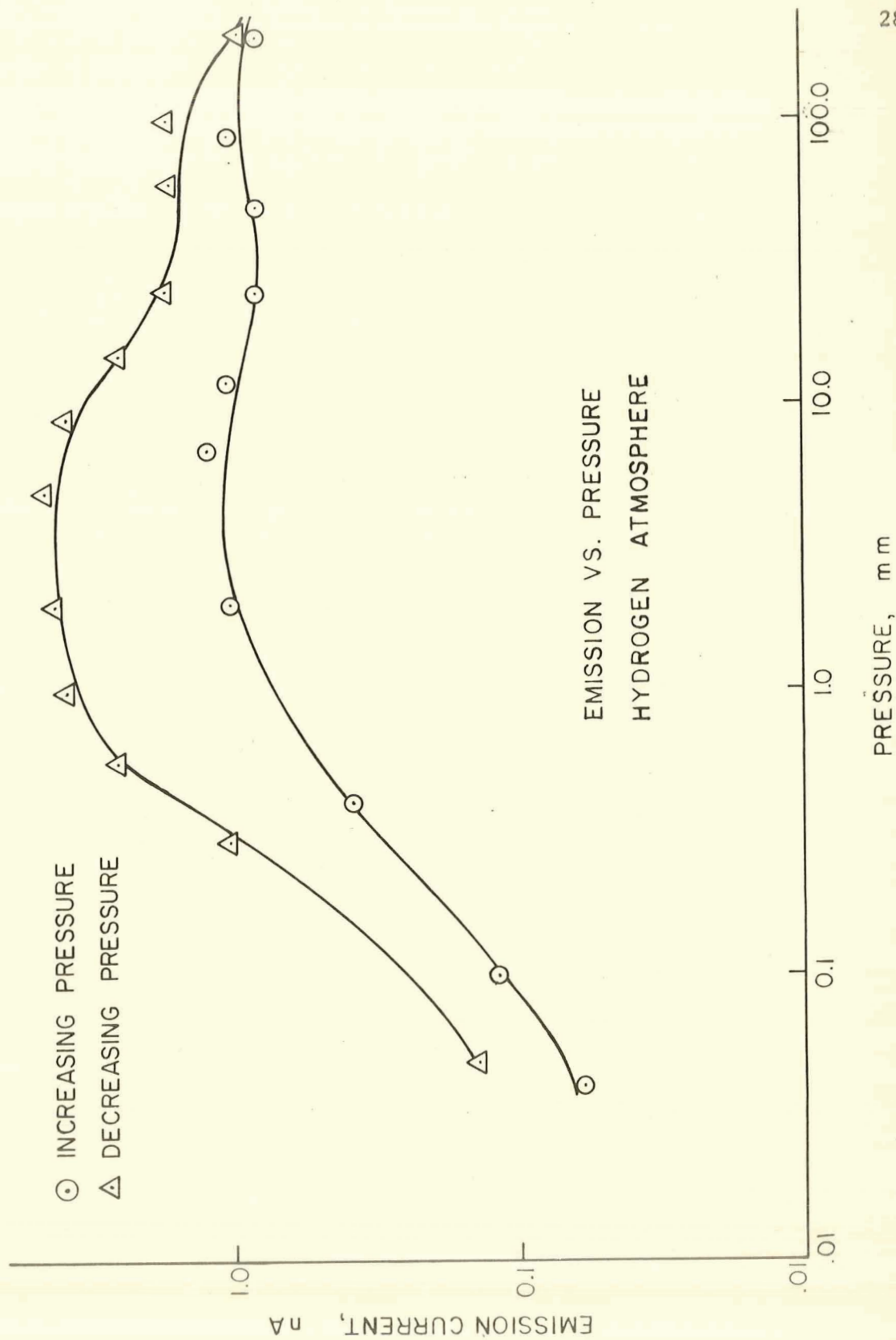


Figure 7. Emission vs. Pressure Hydrogen Atmosphere, Run III

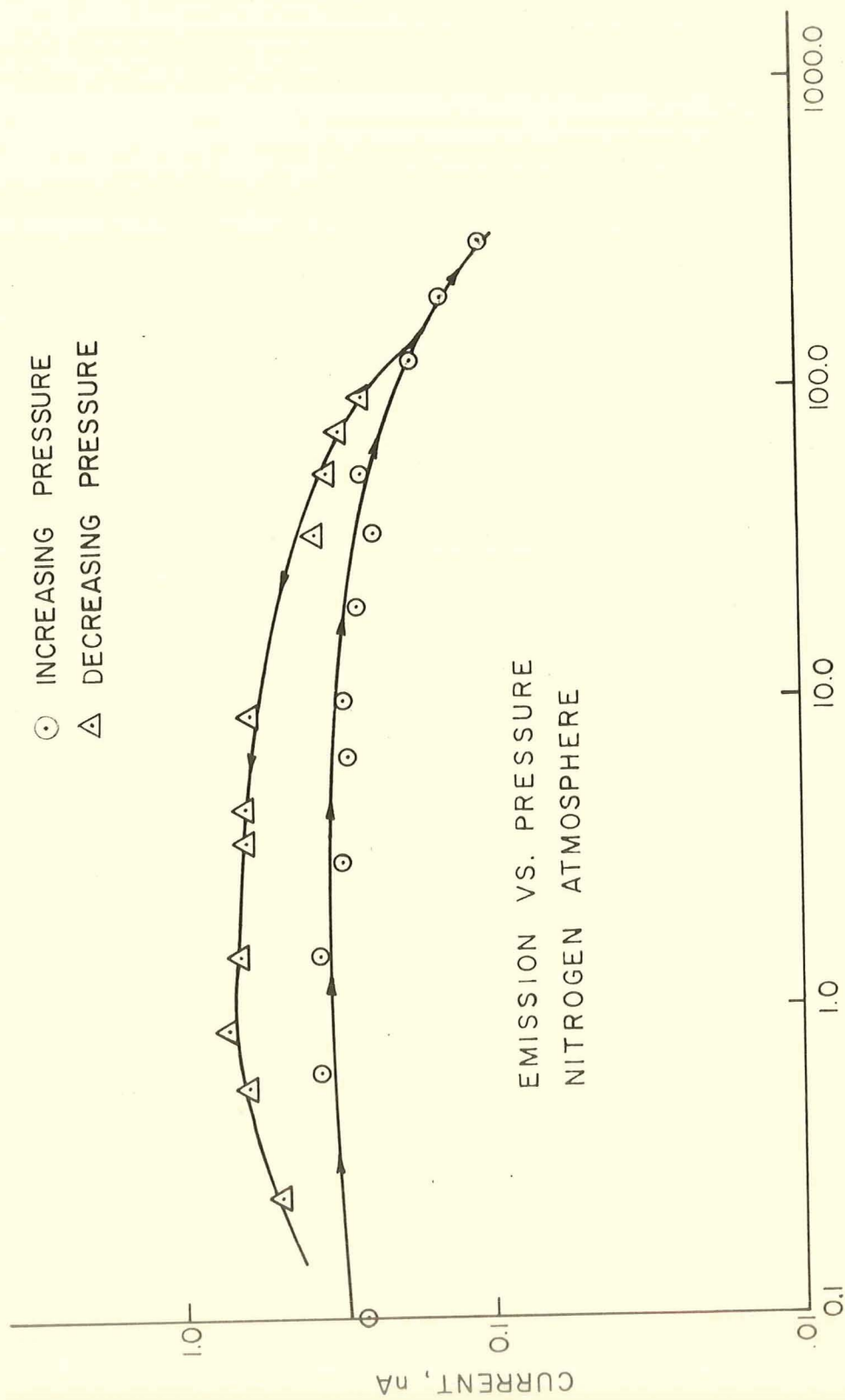


Figure 8. Emission vs. Pressure Nitrogen Atmosphere, Run I

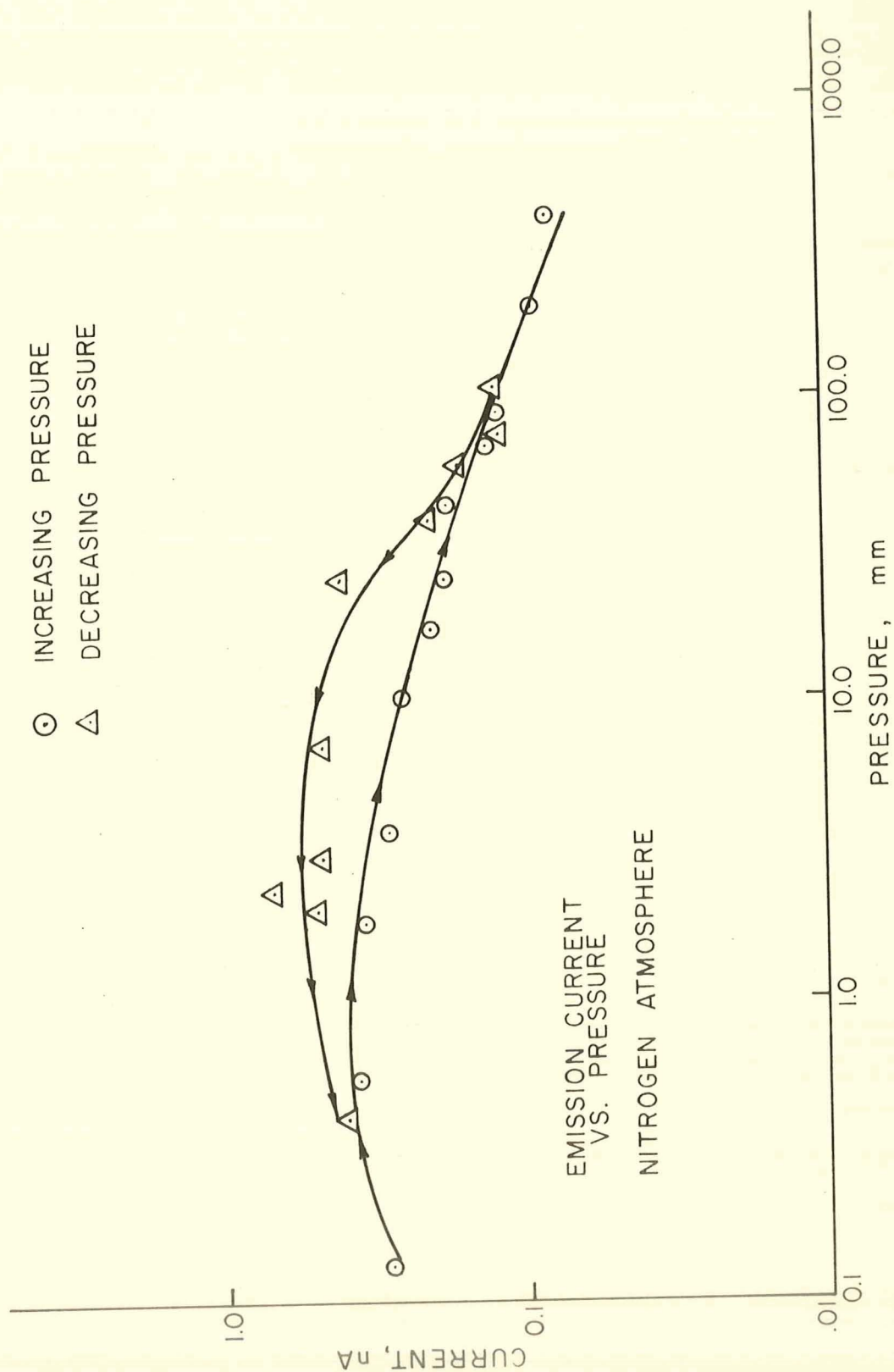


Figure 9. Emission vs. Pressure Nitrogen Atmosphere, Run II

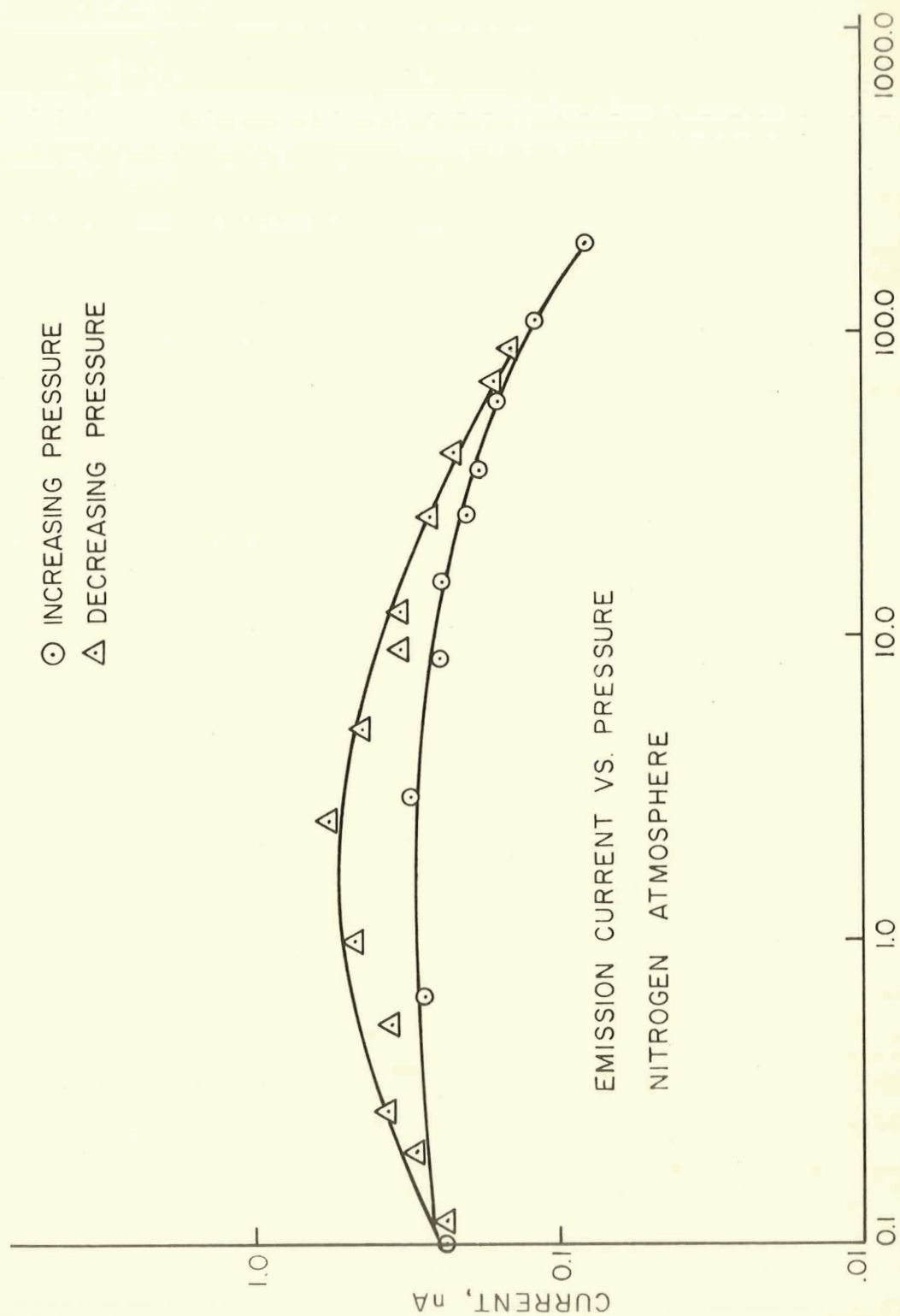


Figure 10. Emission vs. Pressure Nitrogen Atmosphere, Run III

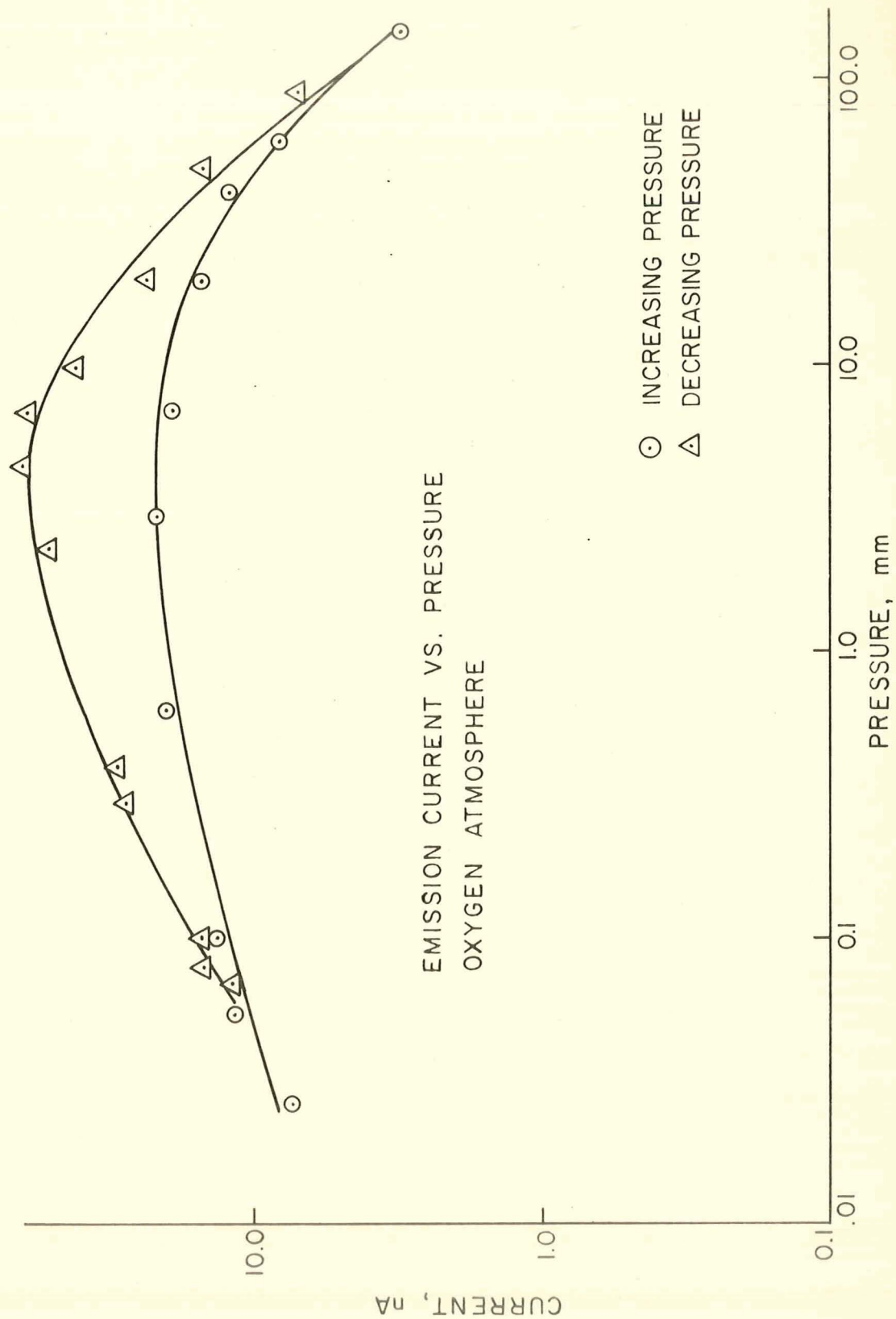


Figure 11. Emission vs. Pressure Oxygen Atmosphere, Run I

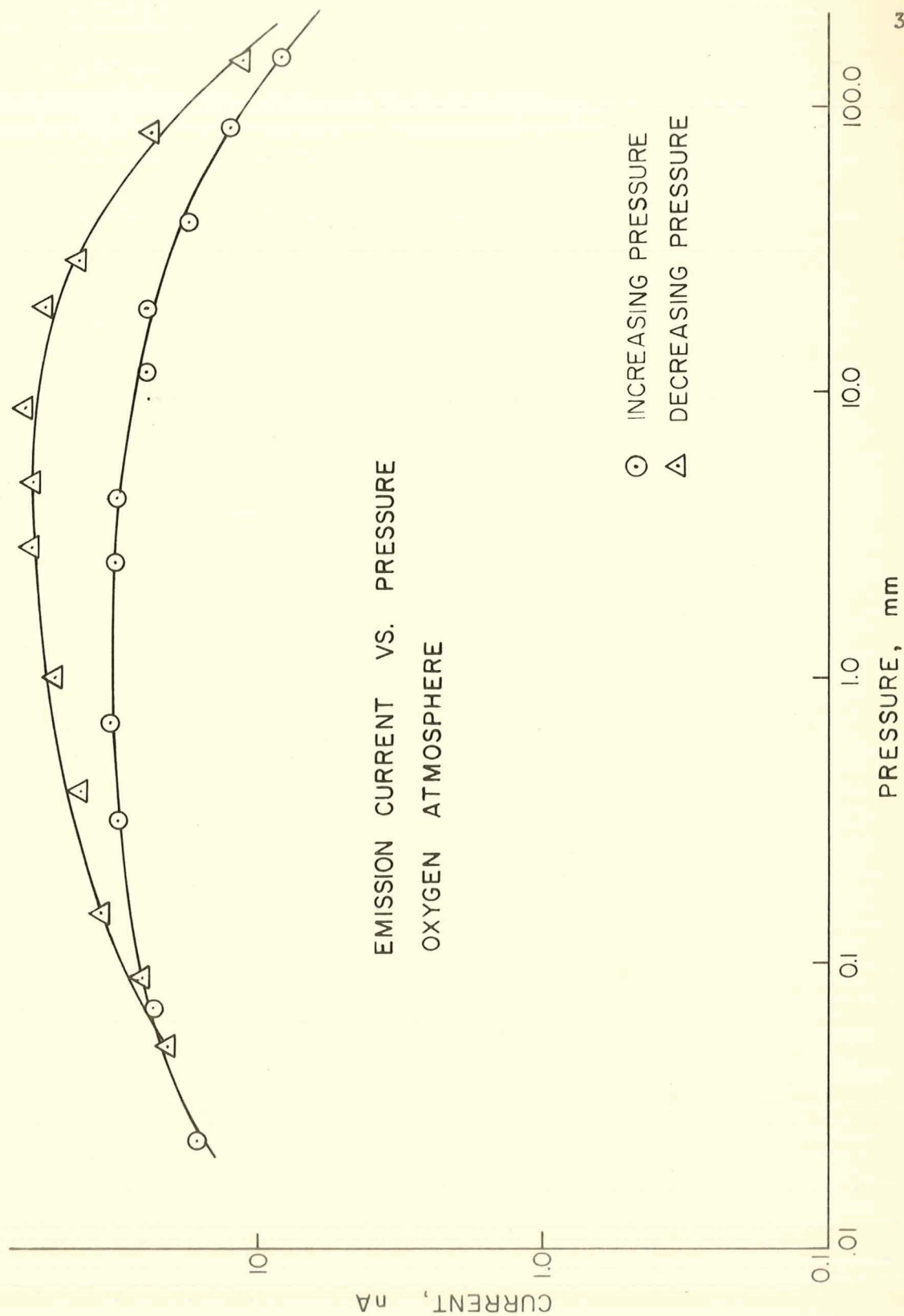


Figure 12. Emission vs. Pressure Oxygen Atmosphere, Run II

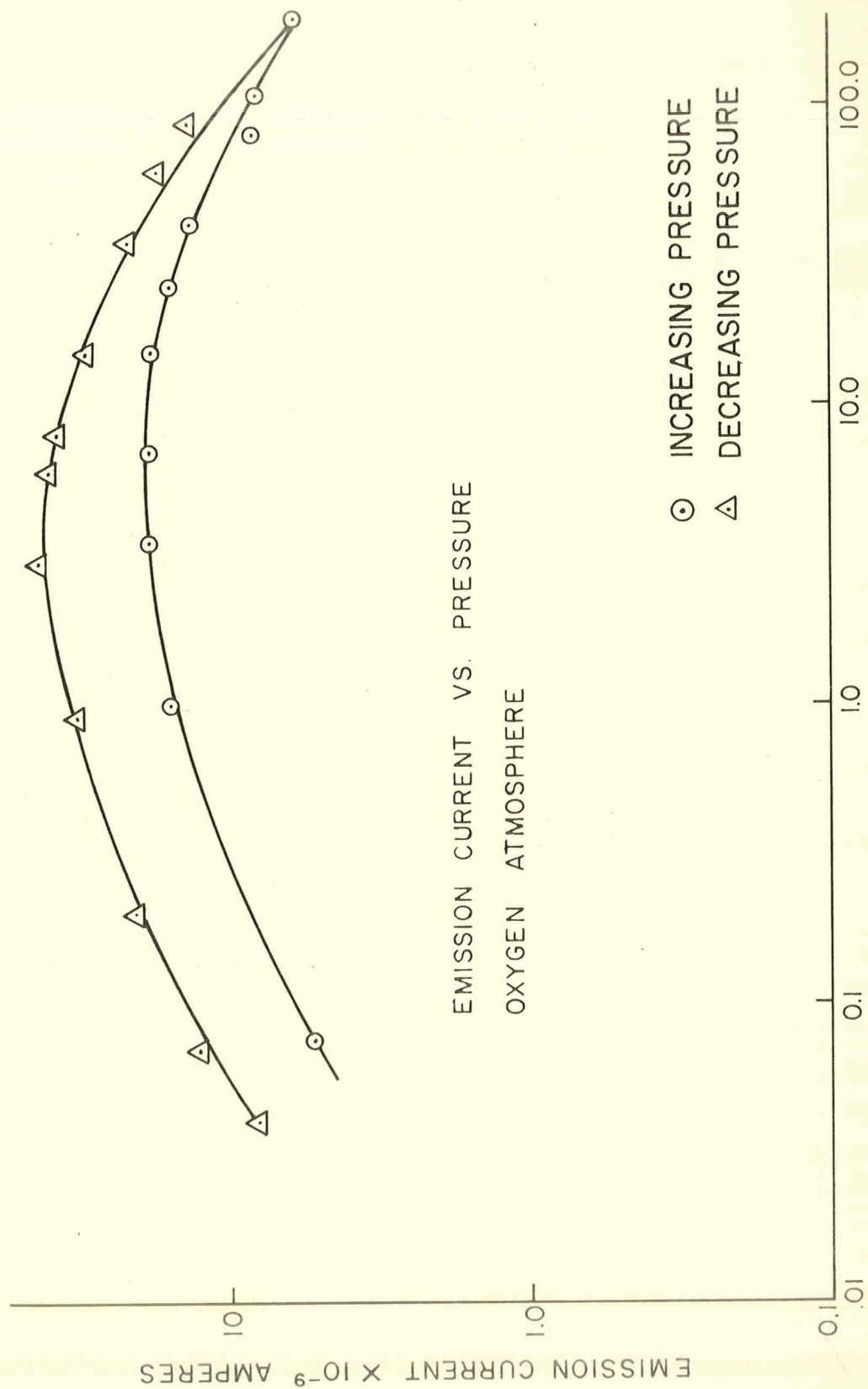


Figure 13. Emission vs. Pressure Oxygen Atmosphere, Run III

of gases in metals. An effect of this type might be expected with hydrogen, which is known to accumulate in palladium (Aston 1966; Brodowsky and Wicke 1966), but the nitrogen and oxygen data is surprising. If these variations are due to solubility and accumulation of these gases in palladium, the resulting expansion of the crystal lattice would cause an increase in the rates of impurity diffusion to the surface, as discussed in Chapter 3.

Effects of Surface Contamination

Significant increases in several mass numbers were found when either hydrogen or carbon monoxide was admitted to the system and the palladium heated to 800°C (Figures 14, 15). Since Palmberg and Tracy (1966) noted that both sulfur and carbon form strongly adherent layers on the surface of palladium, the formation of compounds of sulfur and carbon with ambient carbon monoxide or hydrogen was of particular interest. It was felt that these contaminants could be interfering with the ionization of alkali metals. Removal of the contaminants by reaction with surrounding gases would then be a possible mechanism for controlling positive ion emission.

Exact measurement of the compounds formed was hindered by mass spectrometer drift and by hydrocarbons catalyzed on the hot palladium (Martin and Rummel 1964). To minimize both of these effects each mass peak was normalized by its average peak height for three runs. A delta factor was then defined as the increase in the normalized mass peak height divided by the background mass peak height. The background

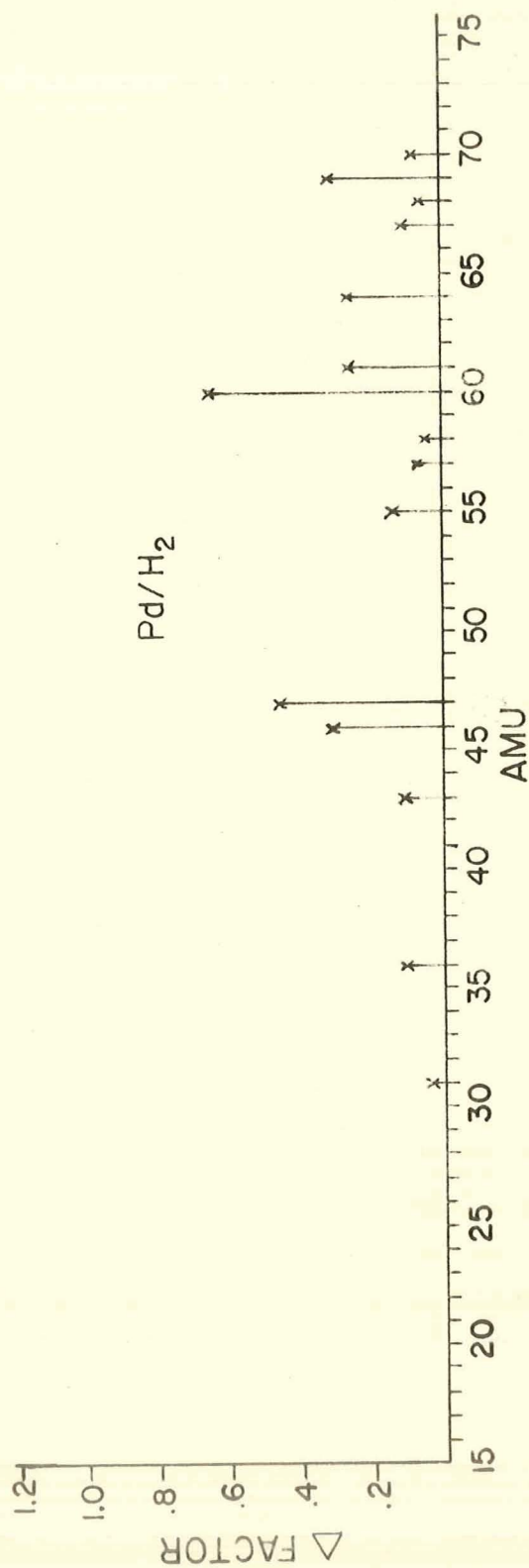


Figure 14. Effects of Gases on Mass Peaks, CO

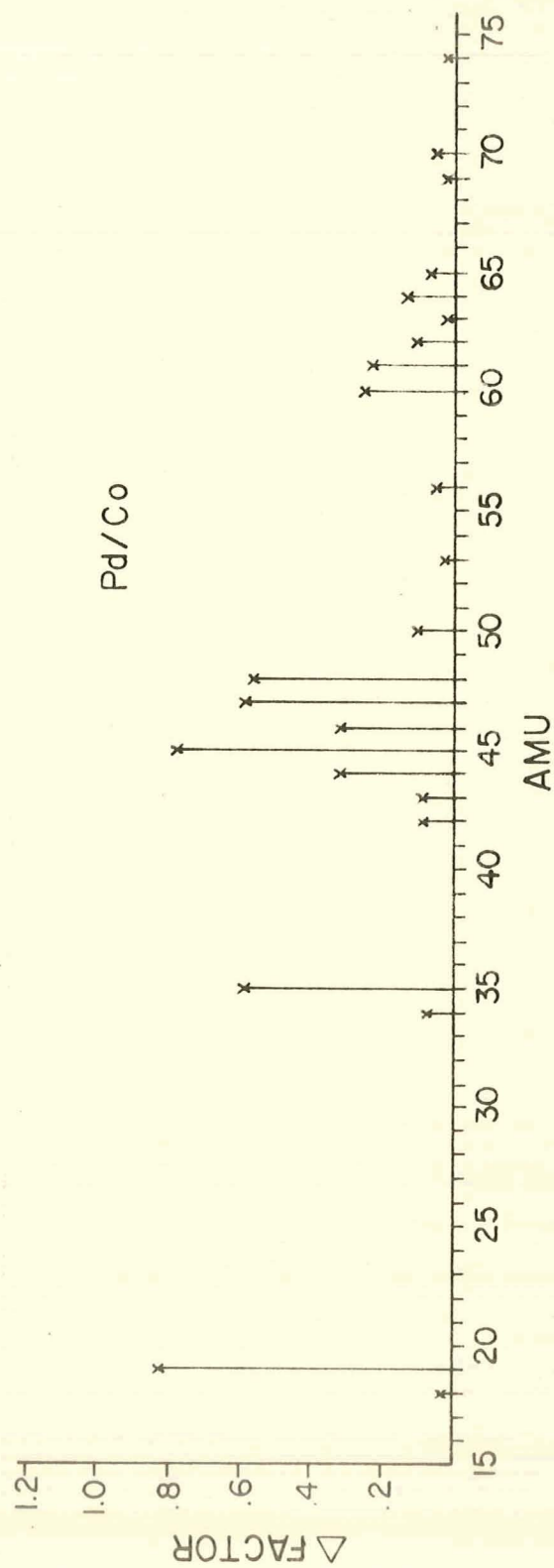


Figure 15. Effects of Gases on Mass Peaks, H_2

mass peak height was the height of each mass peak with the gas in the system but before the palladium was heated. Only the delta factors for mass peaks which increased significantly are shown in Figures 14 and 15.

Most of the peaks shown in the carbon monoxide run are hydrocarbons catalyzed by the hot palladium, however the peaks at 60 and 64 are thought to be COS and SO₂ respectively. These peaks might be C_xH_x compounds catalyzed by the hot palladium but we feel that this is not likely. The background spectra for these runs showed only minimal quantities of any mass peak over 55.

The interesting feature of the delta factors observed with hydrogen was that no hydrogen sulfide, mass 34, was detected; but the increases in masses 60 (COS) and 64 (SO₂) were greater than those observed with carbon monoxide. This could have been caused by the displacement from the palladium of a layer of previously adsorbed carbon monoxide as COS by the more energetic adsorption of the hydrogen. Carbon monoxide is known to be adsorbed in large amounts by palladium in the absence of hydrogen (Taylor and McKinney 1931, Park and Madden 1968).

Although it would be premature to accept this experiment as conclusive, it suggests that CO and H₂ do react with surface contaminants to produce COS and SO₂. The removal of these surface impurities could increase the positive ion emission by changing the work function of the metal and/or permitting more alkali atoms to reach the surface for ionization.

CHAPTER 6

DISCUSSION AND CONCLUSIONS

The experimental results indicate the problems associated with the study of positive ion emission and from hot palladium. These problems are compounded by our limited understanding of surface phenomena.

As yet no definite theory can be proposed for the mechanism controlling positive ion emission. If further work is to be done to determine the applicability of the Saha-Langmuir equation to positive ion emission, clean surfaces must be obtained, possibly by using the method described by Palmberg and Tracy (1966).

Many other areas involved with surface ionization remain to be investigated. The effects of adsorbed gases on emission is still poorly understood, and the effects of changes in the crystal lattice has only been tenuously investigated. In particular, it would be of primary interest to determine if positive ion emission could be used as a sensitive measurement for the investigation of gas-metal solubility.

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